A Quantitative Description of Bragg Analysers

by

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Man wants to know,

and when he ceases to do so,

.

he is no longer man

Fridtjof Nansen 1861-1930

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INTRODUCTION

Von Laue's discovery of the diffraction of X-rays by crystals in 1912 was of great importance in that it helped to confirm the wave nature of X-rays and provided the basis for the demonstration of crystal structure. After the discovery of X-rays by Röntgen in 1895, various workers carried out experiments designed to disclose the nature of X-rays. Particularly noteworthy are Barkla's demonstration of the polarisation of X-rays in 1905, and several rather inconclusive attempts, by Röntgen and later other workers, to diffract X-rays by fine slits. Whilst these experiments indicated that X-rays were a wave phenomenon, W.H.Bragg's interpretation of the ionisation of gases by X-rays as a photoelectric effect suggested a corpuscular nature and thus right up to the end of 1911 there was debate as to the true nature Following discussions with Ewald in early 1912 on interatomic of X-ravs. distances and the properties of short waves in crystals, von Laue proposed that since the wavelength of X-rays and the interatomic distances were thought to be of similar magnitude then the ordered structure of a crystal ought to produce a diffraction effect. He went on to demonstrate this effect and thus confirmed the wave nature of X-rays, as well as demonstrating the internal structure of crystals. Later in 1912 W.L.Bragg interpreted the diffraction of X-rays by a crystal in terms of reflection of the incident X-ray beam by planes of atoms in the crystal and at the suggestion of C.T.R. Wilson demonstrated this by reflecting a beam off a cleaved face of mica.

The first interpretations of X-ray diffraction by von Laue and W.L. Bragg were chiefly concerned with the geometry of the phenomenon and were thus inadequate to determine the intensity or the shape of the diffraction maxima. In 1914, Darwin developed, on the basis of the Bragg reflection concept, a theory that predicted the form of the crystal diffraction profile (or line spread function) and hence the form of the diffraction maxima. The theory, although blemished by its neglect of absorption in the crystal, was innovative in that it allowed for refraction and took account of the interaction between incident and reflected waves within the crystal i.e. the theory was dynamical. Other notable early treatises on X-ray diffraction include a more general dynamical theory by Ewald in 1917 and a development of the latter by Laue in 1931 assuming a 3-d periodic dielectric crystal model. An important innovation to the theory of Bragg reflection is found in the work of Prins in 1930. He modified Darwin's work by introducing a complex refractive index thus taking account of absorption in the crystal. This modification produced a function found to give a very satisfactory quantitative description of Bragg reflection.

Much of the early interest in the clarification of the Bragg reflection phenomenon for its own sake, led to important applications. For instance, W.H. Bragg¹ built the X-ray spectrometer in order to study the X-rays reflected at any angle off a crystal face. However his son W.L. Bragg² used the instrument to determine crystal structure by observing the reflections off different faces of a crystal. In conjunction with this work W.H.Bragg³ studied the spectra of the metals used in the X-ray target and by choosing a suitable crystal face was also able to measure the wavelengths of these spectra. This pioneering work by the Braggs thereby laid the foundations for two important branches of the physical sciences namely, crystal structure analysis and X-ray spectroscopy. It is interesting to note that X-ray spectroscopy came into being at a time when modern atomic theory was in its primary stages so that the early spectroscopic data⁴ on inner shell electron transitions that was made available, played a major role in the determination of the electronic structure of the elements⁵.

The interpretative study of complex X-ray spectra, such as the satellites of strong emission lines and fine structure at absorption edges has been hampered throughout its history by the problem that observed spectra include broadening contributions which reduce the usefulness of the result. Under the most favourable measurement conditions using high resolution Bragg spectrometers the limit to resolving power, in the sense of the Rayleigh criterion of visible optics, is dictated by the width of the crys-In principle, it is possible to make further protal line spread function. gress by resort to any of several available methods to deconvolve this function from the data set. However, such deconvolution clearly requires suitably precise knowledge of this crystal function; the determination of this function with this precision has traditionally presented severe difficulties. In any case even if such a function had been available, then previously the use of it in a deconvolution would have presented a computational task of large proportions. In general therefore spectroscopists have applied approximate deconvolution procedures assuming simple analytical functions for the crystal function. This situation has become increasingly unsatisfactory as spectral measurements have become more precise and demand for more detailed analysis of spectra has become higher. The development of computers over the last fifteen years or so has put a different complexion on this situation in that they provide a means of executing deconvolutions efficiently - particularly with the development of the fast Fourier transform. However the paucity of data for crystal functions is incommensurate with such computational power and thus it would seem worthwhile to pursue the matter of determining these functions. This study proposes a method using computational techniques to obtain a crystal function from a 2-reflection measurement and investigates the usefulness of the method.

Whilst the research topics crystal structure analysis and X-ray spectroscopy have been pursued for more than fifty years now, and are still active, a new impetus was given to the application of Bragg reflection in the mid 1960s. This came from the realisation of the tremendous potential that the technique has for the study of material Radiometric theory predicts that the most powerin the plasma phase. fully emitted wavelengths for an optically thick plasma at about 10^7 K are in the X-ray waveband and furthermore the same result is predicted for an optically thin plasma by atomic theory. Optically thin plasmas, which include all synthetic plasmas and certain important natural plasmas are of particular interest in that the strength of the spectral emission lines of such plasmas can be measured and these strengths in turn can be used to determine source temperature, composition, density and volume. Bragg diffraction analysis of the emission spectra of high temperature plasmas was introduced in the early 1960s, both in the laboratory 6 and space⁷ and is now in widespread use and of increasing importance. Excellent spectra have been recorded by use of large area flat scanning Bragg monochromators⁸ equipped with multiple grid input collimators and gas proportional counters.

The application of Bragg X-ray spectrometry to plasma studies differs somewhat from applications such as X-ray fluorescence spectrometry⁹ and electron probe microanalysis.¹⁰ In material chemical analysis and also other applications like the measurements of atomic energy levels, only the relative (among different wavelengths) efficiency calibrations of the measuring apparatus are required. For applications to material analysis, calibration may be made by use of pre-analysed or synthesized standards. In plasma studies no such standards are available and thus in cases where knowledge of the amount of plasma in the source and hence the absolute power in the beam at each wavelength is required, then quantitative beam power spectrometry must be employed. One now requires really for the first time precision knowledge of the intensity of reflection systematically with wavelength for a wide range of Bragg analy-This thesis reports a comprehensive attack, both by calculation sers. and measurement, on that problem.

One problem encountered in the analysis of the spectra of astronomical plasmas recorded by Bragg spectrometers is that of wavelength calibration. This is a serious matter since for example the spectrum of the solar corona contains emission lines from many elements over a wide range of temperatures (and therefore from elements present in various ionisation states) and thus there is risk of misidentification of lines. A suitable formulation of a wavelength scale for a Bragg spectrometer is given by the Bragg dispersion function, defined in Eqns. (2.1), (2.2), which is a development of the simple Bragg equation (Eqn.1.5) taking into account effects of dispersion and temperature. The pre-calibration of a flight Bragg spectrometer required to determine the Bragg dispersion function is very time consuming and can be avoided by using a selfcalibration technique¹¹ using recognisable lines in the recorded spectrum. Such a technique is normally quite adequate but is subject to uncertainties if there are large, rapid temperature changes during the recording of the spectrum or if there is anomalous dispersion (due to the absorption edge of a constituent element of the crystal) at wavelengths between calibration wavelengths. These problems may be overcome by careful inflight temperature monitoring and a knowledge of the Bragg dispersion function for the For the latter purpose investigations are carried flown spectrometer. out in the present study.

The thesis gives a full account of methods used for measurement and for calculation of Bragg analyser reflection properties and exercises those methods for three typical materials. As an illustration of the new applications of X-ray techniques the thesis closes with two examples of cases in which methods developed here have been applied to serve the research work of others.

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CHAPTER 1

THEORY OF BRAGG REFLECTION

1.1 Introduction

A theoretical knowledge of the magnitude and wavelength dependence of crystal characteristics is important for the following reason. It forms a useful set of guidelines for an experimental measurement program particularly in the selection of measurement wavelengths required to give representative crystal characteristic wavelength dependency plots. The characteristics of any crystal sample are in general dependent upon the degree of crystal perfection of the sample. Therefore, in order to relate measured values to this factor, a comparison of measured values with values derived from theoretical models based on varying degrees of crystal perfection, is required. The two fundamental models adopted are the perfect lattice and mosaic models which are respectively ideally perfect and ideally imperfect limiting cases. An understanding of these models and the calculations based upon them may be obtained from a brief outline of the Bragg reflection theory. The treatment given in this chapter assumes a knowledge of fundamental crystallography as outlined in standard texts.¹²

1.2 Geometry of Lattice Scattering

A crystal is a three dimensional array of atoms in which a group of atoms is repeated at regular intervals in space. It is therefore convenient to think of a crystal as based on a repeating array of points, a lattice, with an identical group of atoms around each lattice point. In 1912 von Laue suggested that since crystal lattice spacings are several times the magnitude of X-ray wavelengths and atoms act as scattering centres then a crystal should act as a three dimensional diffraction grating. A subsequent experiment by von Laue and his collaborators¹³ showed that passing a narrow beam of X-rays through a zinc blend crystal produced on a photographic plate a pattern of spots which corresponded to that expected on the basis of diffraction by a three dimensional grating. This phenomenon led von Laue to propose an explanation of X-ray diffraction.¹⁴

Consider a plane wave of wave vector \underline{k}_0 incident on a line of atoms which form part of a lattice array of atoms with one atom per lattice point. The line of atoms is essentially a linear diffraction grating in which <u>a</u> the vector separation of the atoms is the period of the grating. The radiation will be scattered in all directions but diffraction maxima will only occur in directions in which the phase difference between waves scattered at different atoms is zero. We can thus expect from simple geometrical considerations to predict the condition for constructive interference. Figure 1.1 shows that the phase difference between waves scattered at adjacent atoms is

$$\alpha = (2\pi/\lambda) (OC-AB) = (2\pi/\lambda) ((\underline{a} \cdot \underline{k}_{a}) / |k_{a}| - (\underline{a} \cdot \underline{k}_{o}) / |k_{o}|)$$
$$= 2\pi \underline{a} \cdot (\underline{k}_{a} - \underline{k}_{o})$$
(1.1)

since $|k_a| = |k_o| = 1/\lambda$

The waves will be in phase if

 $a.(\underline{k}_{a} - \underline{k}_{0}) = h \tag{1.2}$

where h is an integer. Equation (1.1) is the well known grating equation which may also be derived for the other two component linear gratings (of periods <u>b</u> and <u>c</u>) of a three dimensional grating. The condition for a diffraction maxima from such a grating is that all three equations are simultaneously satisfied. Thus three equations known as the Laue equations are obtained.

$$\underline{\mathbf{a}} \cdot (\underline{\mathbf{k}} - \underline{\mathbf{k}}_0) = \mathbf{h}$$



Figure 1.1 Geometry of the phase difference between waves scattered by two adjacent atoms



Figure 1.2 Geometry of diffraction based on Bragg's model



Figure 1.3 The relationship of the components of the electric vector of scattered electromagnetic radiation at P to the components of the electric vector of the incident radiation at O

$$\underline{\mathbf{b}} \cdot (\underline{\mathbf{k}} - \underline{\mathbf{k}}_0) = \mathbf{k}$$

$$\underline{\mathbf{c}} \cdot (\underline{\mathbf{k}} - \underline{\mathbf{k}}_0) = 1$$
(1.3)

The integers h, k and l may be shown to be the Miller indices of a family of lattice planes (Ref.15, p.31) from which diffractions arises. <u>k</u> is the wave vector of the wave diffracted from this family of planes. The three Laue equations may also be written as the single vector equation. (Ref.16, p.84)

$$\underline{\mathbf{k}} - \underline{\mathbf{k}}_{\mathbf{0}} = \underline{\mathbf{G}} \tag{1.4}$$

where <u>G</u>, a reciprocal lattice vector, is normal to the diffraction planes and has a magnitude $1/d_{hk1}$ which is the reciprocal of the spacing of the diffraction plane (Ref.15, p.17). It may be expressed as <u>G</u> = h<u>a</u>* + k<u>b</u>* + 1<u>c</u>* where <u>a</u>*, <u>b</u>*, <u>c</u>* is the vector set reciprocal to <u>a</u>, <u>b</u>, <u>c</u>. Since <u>G</u> is perpendicular to the diffracting planes and $|\underline{k}| = |\underline{k}_0|$ a simple geometrical interpretation of the occurence of diffraction maxima may be given as shown in Fig.1.2. The vectors <u>k</u> and <u>k</u>₀ make equal angles with the diffracting planes and therefore the diffracted beam can be considered to be the result of reflection of the incident beam by the stack of diffracting planes. Bragg adopted this informal approach to X-ray diffraction by explaining the spot patterns of Laue's experiment in terms of reflection of an X-ray beam by planes of atoms. For the sake of introducing Bragg's model the planes shown in Fig.1.2 can be considered as planes of atoms of Miller indices (h, k, l). †

+ A distinction must be made between rational and non-rational planes. The former type have a real existence in the sense that they correspond to planes of atoms in the crystal whilst the latter type are imaginary planes associated with nth order reflections from a rational plane. The Miller indices (h, k, l) of a rational plane have no common factor. The Miller indices of an nth order reflection may be expressed as nh, nk, nl. For the sake of convenience, in the general formulation of diffraction phenomena the two kinds of indices are distinguished by the use of parenthesis for indices representing a rational plane and no parenthesis for indices representing a reflection, viz (h, k, l) and h, k, l respectively.

Unlike specular reflection the reflected beam is produced only at certain values of the glancing angle θ . These values are governed by the condition that the waves from different planes must be in phase i.e. the path difference between the waves must be an integral number of wavelengths. From Fig. 1.2 this may be expressed as

$$n\lambda = AB + BC$$

which expressed in terms of the plane spacing $d_{(hk1)}$ gives

$$n\lambda = 2d_{(hkl)}\sin\theta_{n(hkl)}$$
(1.5)

where n is the order of diffraction. The relation, known as Bragg's Law, may also be derived from Laue's treatment by equating the magnitudes of the two sides of Eqn. (1.3). It is clear, from Fig.1.2, that $|\underline{k}-\underline{k}_0| = 2\sin \frac{6}{\lambda}$ and from standard texts (<u>G</u>) = $1/d_{hkl}$ or expressing this explicitly in terms of the reflection order (<u>G</u>) = $1/d_{nh}$, nk, nl = $n/d_{(h, k, l)}$.[†]

This section has emphasized that the phenomenon observed by Laue is one of diffraction but can be looked upon in terms of reflection of X-rays from a stack of atomic planes. This latter viewpoint is based on the simple Bragg model to which there will be recourse since it lends itself to the discussion of X-ray scattering at crystal surfaces.

Whilst the condition for constructive interference has now satisfactorily emerged from simple geometry, of course physical models and their algebraic description will now be needed to described the strength of the diffracted beams.

1.3 Atomic Scattering

1.3.1 Definition of the atomic scattering factor in terms of electron scattering The interference maxima of Bragg reflection arise from the radiation

⁺ It is common practice to merge the reflection order with the Miller indices. Bragg's Law which becomes $\lambda = 2d_{nh,nk,nl} \sin \theta$, is expressed in this form in the computer programs used in this study.

scattered by atoms associated with the lattice points of a crystal. A knowledge of the characteristic ratio of the scattered and incident wave amplitudes associated with each atom type is fundamental to the determination of the magnitude of the interference maxima. Almost all the scattering of an atom is done by the electrons and therefore it is instructive to consider briefly scattering by a free electron. Thomson¹⁸ calculated the scattering by a free electron on the basis of classical electrodynamic theory and thus predicted only the scattering of coherent radiation i.e. scattered radiation of the same wavelength as the incident radiation. Whilst electrons in atoms do not behave as free electrons and wave mechanical theory must be introduced to predict incoherent scattering, Thomson's theory is nevertheless worth considering because the derived scattering intensity of an electron provides a convenient unit of scattering.

Consider a beam which travels along the path OX (see Fig. 1.3) and impinges on an electron at O. In order to determine the nature of the scattered wave at point P which is a distance r from O it is useful to resolve the electric vector E_0 of the incident beam into two components E_{0y} and E_{0z} which are respectively parallel and perpendicular to the plane OXP. The electric vector components of the scattered wave at P are given according to Thomson by

$$E_z = -(e^2/(mc^2 r)) E_{0z}$$
 (1.6)

$$\mathbf{E}_{\mathbf{v}} = -(\mathbf{e}^2/(\mathbf{m}\mathbf{c}^2\mathbf{r}))\mathbf{E}_{\mathbf{o}\mathbf{v}}\cos\theta_{\mathbf{c}}$$
(1.7)

where θ_{S} is the scattering angle.[†] The resultant electric vector of the

⁺ It is convenient in future expressions to introduce a polarisation coefficient p with unit value for the electric vector component perpendicular to the plane of scattering (σ - polarisation) and value |cos2 θ| for the electric vector component parallel to the plane of scattering (π - polarisation).

scattered wave is given by

$$E^{2} = E_{z}^{2} + E_{y}^{2}$$
(1.8)

If the incident beam is unpolarised

$$E_{oy}^{2} = E_{oz}^{2} = \frac{1}{2} E_{o}^{2}$$
 (1.9)

Since the intensity of the incident and scattered beams I_0 and I respectively are proportional to the square of their electric vectors Eqns (1.6) to (1.9) may be combined to give

$$I = I_0 \left[\frac{e^4}{(m^2 c^4 r^2)} \right] \left[(1 + \cos^2 \theta_s) / 2 \right]$$
(1.10)

This relation is called the Thomson scattering equation. The factor($1+\cos^2\theta_s$)/2 is called the polarisation factor for an unpolarised primary beam.

Atomic scattering is quantitatively defined in terms of electron scattering as follows: the atomic scattering factor f is the ratio of the scattered amplitude due to a given atom to that due to a single classical electron under identical conditions. The scattering factor may be more explicitly designated f (θ_s, k) where $k = 2\pi/\lambda$.

Since it is the electrons of an atom that give rise to scattering the development of the calculation of atomic scattering factors has gone hand in hand with the development of atomic theory. These parallel developments are outlined below.

1.3.2 The calculation of atomic scattering factors

a. Early developments

The very earliest treatments of X-ray diffraction by Laue and Darwin took account of atomic scattering and indeed Darwin realised that atomic scattering power depended on the spatial distribution of electrons in an atom. The first calculations of atomic scattering were based on classical electron scattering theory and classical atomic theory, the latter assuming the concept of instantaneous electron configurations in the atom. According to classical scattering theory each electron is so loosely bound in the atom that it may be regarded as a free electron for which scattering intensity is given by Thomson's formula (Expression (1.10)). It is assumed that the electron orbital dimensions are similar to the atomic dimensions and the wavelength of the incident radiation; consequently in the forward direction f - Z the atomic number but for $f_S \neq 0$ phase differences will arise between the scattered waves from electrons in different parts of the atom and thus f will decrease with increasing angle of scattering. Since electron distributions vary from one atom type to another so the f, θ_S dependency will also differ.

The scattering factor may be calculated from classical theory in terms of N atoms arranged in a crystal lattice (Ref. 21 Chapter 3). First consider that each atom in the crystal contains a single electron. An average is taken over the instantaneous positions of the electrons by assuming the crystal to be a composite atom that contains all the electrons. The probability that an electron lies within a given element of the composite atom is N times the probability that one lies within the corresponding element of volume of a single atom chosen at random. Let $\rho(\underline{r}) d\tau$ be the probability that an electron in any atom lies within a volume element $d\tau$ whose position with respect to the atom is given by the vector \underline{r} . Then the amplitude scattered by the composite atom is

$$N \left| \rho(\underline{r}) e^{i\phi} d\tau \right|$$
 (1.11)

where ϕ is the phase difference arising from a given electron being noncoincident with an atom centre and hence also with a lattice point. The integral is taken over the volume of a single atom. Expression (1.11) shows that the scattering amplitude for the whole lattice may be expressed in terms of each lattice point being occupied by an atom scattering f times the amplitude

scattered by a single electron, where

$$f = \int \rho(\underline{r}) e^{i\phi} d\tau \qquad (1.12)$$

The classical treatment assumes the average atom to be spherically symmetrical and thus derives the following

$$f = \int_{0}^{\infty} U(r) \sin \mu r / \mu r \, dr \qquad (1.13)$$

where U(r) dr is the probability that an electron lies between radii r and r + dr in any atom, $U(r) = 4\pi r^2 \rho(r)$ and $\mu = 4\pi (\sin \theta) / \lambda$. For multielectron atoms it is necessary to define radial probability functions $U_1(r) \dots U_Z(r)$ which give the probability that in any atom electrons of any given type lie between the radii r and r + dr. Hence U(r)dr in (1.13) becomes $U(r) dr = \sum_{n} U_n(r) dr$.

The classical theory of atomic scattering falls short in that it treats only coherent scattering whereas in reality incoherent or Compton scattering²² occurs and contributes to background scattering. Compton²³ formally introduced incoherent scattering into the classical theory using the classical formula for the intensity scattered per atom by a monatomic gas which is given by

$$I = \sum_{n} (1 - f_{n}^{2}) + f^{2}$$
(1.14)

where f_n is the scattering factor of a given electron in an atom and the summation is over all electrons in the atom. He suggested that the term f^2 arises from coherent scattering and the term $\sum_n (1 - f_n^2)$ from incoherent scattering. Quantum theory showed this to be formally correct but nevertheless this interpretation was rather arbitrary. Clearly more sophisticated treatments were required for dealing with atomic scattering.

b. The high frequency limit

Early calculations of atomic scattering factors based on classical scattering theory adopted the assumption that the frequency of the incident radiation was much greater than the natural frequencies of the electrons. This allowed a simple calculation of scattering factors valid to within the conditions of the assumption. Later calculations by wave mechanical methods derived atomic scattering factors taking account of scattering for incident radiation frequencies close to characteristic electronic frequencies and treated the calculation for high frequency incident radiation as a limiting case. Atomic scattering factors thus required a numerical form consisting of the sum of the two types of terms, a constant frequency independent term (the high frequency limit term) associated with normal dispersion and frequency dependent terms associated with anomalous dispersion. The calculation of the frequency independent term is discussed below and the frequency dependent terms in Subsection 1.3.2.c.

<u>i. Semi-classical approach</u> Hartree²⁴ made the first attempt at determining the high frequency limit atomic scattering factor designated f_0 by calculating the classically derived radial probability function U(r) on the basis of Bohr atomic theory. This theory, the cornerstone of the old quantum theory, regarded the electrons of an atom as being in discrete energy states and orbitals. Hartree estimated the orbital dimensions from X-ray and optical data and using the time - average method outlined in Subsection 1.3.2.a obtained U(r) from which f_0 was calculated by numerical integration of Eqn.(1.13). Comparison of experimental and calculated curves of $f_0((\sin\theta)/\lambda)$, where $\theta = \theta_S/2$ showed systematic deviations, in particular, humps in the calculated curves for low angles. Nevertheless Hartree's calculations provided a useful indication of the magnitude and θ dependency of scattering factors.

ii. Wave mechanical method The calculation of atomic scattering factors using classical scattering theory with the Bohr atomic model gave values of the right order but the method was theoretically unsound. It was only the advent of modern quantum theory that allowed proposition of a unified theory

 25,26 of scattering. The quantum theory of scattering differed fundamentally from classical theory in that implicit in classical theory was the assumption of exact determination of electron configurations whereas according to quantum theory only the probability of finding an electron in a given region could be determined. The quantum theory used the method of wave mechanics to set up a wave equation appropriate to a particular atom under consideration. Schrödinger ²⁷ derived from the wave equation, an expression of the same form as the equation derived from electrical theory which relates charge density ρ to current density <u>j</u>. This latter equation is given by

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \underline{j} = 0 \tag{1.15}$$

The terms derived by Schrödinger corresponding to ρ and <u>j</u> are called the Schrödinger charge density and current density. One method of treating atomic scattering is to regard the atom, in the absence of incident radiation, to be in a stationary state such that the Schrödinger charge and current density are time-independent. The incident radiation is then regarded as a perturbation of the atomic field that causes periodic variations of the current density which give rise to scattered radiation. The scattered radiation is then calculated from the laws of classical electrodynamics for a current distribution undergoing periodic variation. Full accounts of the method are given in Ref. ²¹ and wave mechanical texts. It is important to note that for the high frequency limit case the current density is proportional to the charge density and that $f_{n,n}$ the scattering factor for coherent radiation for an atom containing one electron in the state n is given by

$$\mathbf{f}_{n,n} = \int |\psi_n|^2 \, \mathrm{e}^{\mathrm{i}\phi} \, \mathrm{d}v \tag{1.16}$$

where ψ_n is a wavefunction associated with u the solution of the wave equation. The scattering factor for the whole atom may be obtained by summing Eqn.(1.16) over all electrons in the atom assuming that the

total wavefunction may be expressed as a product of Z individual electronic wavefunctions. Equation (1.16) differs from Eqn.(1.12) in that the probability $\rho(\mathbf{r})$ is replaced by the probability $|\psi_n|^2$ calculated by wave mechanical methods. In effect this means that $\mathbf{e}|\psi_n|^2$, the Schrödinger charge density is treated as a classically scattering charge density, ψ_n being so normalised that $\int |\psi_n|^2 d\mathbf{v} = 1$, so that the probability of finding an electron somewhere is unity. The radial probability function U(r) of (1.13) now becomes equal to $4\pi \mathbf{r}^2 |\psi_n|^2$. The wave mechanical theory takes account of incoherent scattering by associating it with transitions from one atomic state to another.

The quality of f-values calculated by wave mechanical methods will depend upon the assumptions and approximations used in formulating the wave equation. Early forms of the equation were based on the assumption that only the nuclear field acted on the electrons of an atom. This assumption took no account of the field acting on a given electron due to the other electrons in the atom. Hartree²⁸ included the effect of other electrons by representing it as part of the central field. The problem for the atom was thus expressed in terms of Z independent wavefunctions which allowed for the interaction of electrons. Ψ the total wavefunctions is used in the method outlined above to calculate the atomic scattering factor. In order to calculate the individual electron wavefunctions Hartree used the self consistent field method. This involves estimating from atomic theory the field V(r) acting on an electron. This 'initial' field value is then used in the radial' wave equation for an electron in a central field, given by

$$\frac{d^2 P}{dr^2} + \left[\frac{2m}{\hbar^2} \left\{ E - V(r) \right\} - \frac{\ell(\ell + 1)}{r^2} \right] P = 0 \qquad (1.17)$$

where $P = r\psi$ the radial wavefunction, E is the energy of the electron and ℓ is the angular momentum quantum number. Equation (1.17) is integrated using a trial value of E which is adjusted such that the solution exponentially goes to zero for large r. The integration gives a value of P which may be used to determine the contribution of an (n, ℓ .) electron group to the total potential V(r) and this is compared with the assumed contribution of this group to the initial V(r). If there is a discrepancy, the initial field value must be adjusted to give self consistency. This procedure is carried out for each electron group.

Fock²⁹ and Slater³⁰ independently developed Hartree's method by suggesting that since individual electrons cannot be identified then Ψ should be expressed in a determinant form to take account of the exchange principle. The best value of Ψ may be determined by the variation method which leads to a set of simultaneous differential equations for the electronic wavefunctions. The equations, called the Hartree-Fock (HF) equations, may then be solved by a method analogous to the self consistent field method. The Hartree-Fock method requires considerable computational labour because each electron moves in a slightly different potential field and so must be treated as a separate problem. Slater simplified this method by setting up an average potential field in which, it was considered, all electrons moved. Furthermore the exchange charge (the charge removed from the total field to give the field acting on a single electron) was replaced by the corresponding value for a free-electron gas whose local density is equal to the density of actual charge at the position in question. This simplified method for calculating scattering factors became known as the Hartree-Fock-Slater method.

It should be noted that the methods outlined ignore spin and relativistic effects, the latter being particularly relevant to scattering by heavy atoms

and when the incident radiation frequency is very high. Cromer and Mann³² comment in their comparison of the Hartree-Fock-Slater, Thomas-Fermi-Dirac, Hartree and Dirac-Slater models that, apart from relativistic effects, the HF model is the best free atom approximation and HF scattering factors may be used for atoms lighter than Cs (Z = 55).

c. Frequency dependent terms

When the frequency of the radiation incident on an atom j approaches characteristic electronic frequencies, anomalous scattering occurs because frequency dependent quantities that contribute to the scattering factor become significant. The required generalised form of the scattering factor is given by

$$\mathbf{f}_{j} = \mathbf{f}_{0,j} + \Delta \mathbf{f}_{j}' + i\Delta \mathbf{f}_{j}'' \tag{1.18}$$

where f_0 is the frequency independent term and $\Delta f'$ and $\Delta f''$ are respectively the real and imaginary frequency dependent terms of the scattering factor. Since the refractive index of a material is related to the scattering factors of the constituent atoms (see Subsection 1.6.2.b) anomalous dispersion occurs, hence $\Delta f'$ and $\Delta f''$ are commonly referred to as the real and imaginary anomalous dispersion terms. The high frequency constraint hitherto imposed on the calculation of scattering factors must now be removed to allow calculation of the anomalous dispersion terms.

i. Screened hydrogenic approximation To begin the calculation it is noted that, on the Bohr model, each atom has characteristic frequencies corresponding to transitions of each electron from its ground energy to any higher unoccupied bound state or to the positive continuum. On this semiclassical model one can expect the frequency dependent scattering terms, which are now sought, to be significant only where the incident radiation frequency is of the order of one of those characteristic frequencies. Further, it is easily shown from the Bohr model, that the wavelengths corresponding to these characteristic frequencies are always very much larger than the radius of the (rest energy) Bohr orbit of that electron. Under these conditions the calculation may regard the scattering electron as a dipole oscillator, albeit with a large set of characteristic frequencies. The frequency dependent terms have significant values only under conditions where the dipole assumption is a close approximation to reality; no such restriction applies to the calculation of the frequency independent term (see below). A wave mechanical exposition easily confirms this argument and, indeed, allows calculation of those higher order frequency dependent multipole terms and shows them always to be small. On this Bohr model, the semi-classical result for the scattering factor of a bound electron is easily found, see for example Ref ²¹, as

$$p f_{q}(\omega) = p \int_{\omega_{q}} [\omega^{2} (dg/d\omega_{s})_{q}/(\omega^{2} - \omega_{s}^{2} - i\kappa_{q}\omega)]d\omega_{s} \qquad (1.19)$$

where q specifies the quantum numbers of the particular electron considered. ω is the angular frequency of the incident radiation. ω_s is the resonance angular frequency of a particular hypothetical classical dipole which is one of a set, distributed in frequency with density $(dg/d\omega_s)_q$ near ω_s , and whose aggregate scattering behaviour simulates that of a single q-type electron.

 ω_q is the angular frequency corresponding to a transition of the q-type electron from its bound state to the first vacant excited state.[†] κ_q is a factor included in the equation which describes the motion of each oscillator and which describes the net effect of damping mechanisms. p is an angular

⁺ More generally the integration should be shown over all frequencies, but ω_q is the first frequency at which $(dg/d\omega_s)_q$ has significant value. Note that the standard texts usually take ω_q as the frequency corresponding to excitation to zero energy. It is better to take this as an approximation which is useful in some cases but not in general.

factor which depends upon the inclination of the radiation polarisation to the scattering plane. This factor may be normalised from the definition of the scattering factor and shown explicitly as the polarisation coefficient in final results e.g. Eqns. (1.65), (1.73). Then for each atom of type j,

$$\mathbf{f}_{j}(\omega) = \sum_{q} \mathbf{f}_{q}(\omega)$$
(1.20)

Rationalising expression (1.19),

$$f_{q}(\omega) = f'_{q}(\omega) + i\Delta f''_{q}(\omega)$$
(1.21)

where

$$f'_{q}(\omega) = \int_{\omega_{q}}^{\infty} \left[\left[\left[\omega^{2} (\omega^{2} - \omega_{s}^{2}) (dg/d\omega_{s})_{q} \right] / \left[(\omega^{2} - \omega_{s}^{2})^{2} + \kappa_{q}^{2} \omega^{2} \right] \right] d\omega_{s}$$
(1.21a)

i.e.

$$f'_{q}(\omega) = f'_{0q} + \Delta f'_{q}(\omega)$$
 (1.21b)

where

$$\mathbf{f}_{0q}^{'} = \int_{\omega_{-}} \{ (\mathrm{d}g/\mathrm{d}\omega_{s})_{q} \} \mathrm{d}\omega_{s}$$
(1.21c)

and

$$\Delta f_{q}'(\omega) = \int_{\omega_{q}}^{\omega} \left[\left[\left[\omega_{s}^{2}(\omega^{2} - \omega_{s}^{2}) - \kappa_{q}^{2}\omega^{2} \right] (dg/d\omega_{s})_{q} \right] / \left[\left[\left(\omega^{2} - \omega_{s}^{2} \right)^{2} + \kappa_{q}^{2}\omega^{2} \right] \right] d\omega_{s} \right]$$
(1.21d)

and also

$$\Delta f_{q}''(\omega) = \int_{\omega_{q}} \left[\left[\kappa_{q} \omega^{3} (dg/d\omega_{s})_{q} / \left[(\omega^{2} - \omega_{s}^{2})^{2} + \kappa_{q}^{2} \omega^{2} \right] \right] d\omega_{s}$$
(1.21e)
The term (1.21c) is just the oscillator strength of a q-type electron. For

 $\omega >> \omega_s$ both Expressions (1.21d) and (1.21e) vanish and the only contributions to the summation (1.20) are terms like (1.21c) which then total to the element atomic number Z, i.e. they reduce to total to the dipole value of $f_0(\theta_s, k)$ (i.e. the value for $\theta_s = 0$), as expected. As noted above, though the dipole approximation may be justified for calculation of both $\Delta f'_q(\omega)$ or $\Delta f''_q(\omega)$, wherever their values are significant compared with that of $f(\theta_s, k)$, this approximation is not generally justified for the frequency independent part. Therefore in all that follows we replace the summations (1.20) of terms like (1.21c) by the Hartree-Fock results of Ref. 32. Next, it is noted that for any plausible value of κ_q the integrand of (1.21e) differs significantly from zero only when ω very nearly equals ω_s^+ so that (1.21e) may be written as

$$\Delta f_{q}^{\prime\prime}(\omega) \simeq \frac{1}{2} \kappa_{q} \omega^{2} (dg/d\omega_{s})_{q} \int_{0}^{2} \omega_{s} d\omega_{s} / [(\omega^{2} - \omega_{s}^{2})^{2} + \kappa_{q}^{2} \omega^{2}] \qquad (1.21f)$$

where in this small significant range we take $(dg/d\omega_s)_q$ as effectively constant and $\omega \simeq \omega_s$ in the first power but not in the second power. Then

$$\Delta f''_{q}(\omega) \simeq \frac{1}{2} \kappa_{q} \omega^{2} (dg/d\omega_{s})_{q} \cdot \pi/\kappa_{q} \omega = (\pi/2) \omega (dg/d\omega_{s})_{q} \qquad (1.21g)$$

and independent of the precise value of the damping constant, so long as its value is small in the context defined.

At this point the semi-classical calculation essentially fails because neither classical physics nor old quantum theory quantitatively defines the hypothetical function $(dg/d\omega_g)_q$ and it is usual to make appeal to empirical data (in fact to absorption coefficients) to find values of this function. However, it is noted that a wave mechanical exposition results in expressions which may be given formally identically with (1.19) through (1.21) in which the oscillator density is given as matrix elements of the ground and excited wavefunctions. Given the oscillator density function, either from the wavefunctions or from empirical data, insertion in (1.21) followed by numerical integration and the summation (1.19) is sufficient to find the solution in any case. However, inspection of particular cases reveals the possibility of substantial simplifying approximations which allow further analytical progress and thus relieve the computation time needed. First it is noted that from (1.21d) and (1.21e),

both $\Delta f'_q(\omega)$ and $\Delta f''_q(\omega)$ go to zero for $\omega \gg \omega_q$. In circumstances

[†] The condition for this is simply that $\kappa_q^2 \omega^2 << (\omega^2 - \omega_s^2)^2$ except when $\omega \simeq \omega_s$. By inspection of (1.21e) even an upper limit of κ_q at 10⁻³ illustrates how very closely the condition is met.

where $\omega > \omega_{q}$ and where the range of ω/ω_{q} for which $\Delta f'(\omega), \Delta f''(\omega)$ are required is always restricted as $(\omega/\omega_{q}) \neq 1$ inspection of (1.19) shows that no plausible value of κ_{q} can produce results for $\Delta \hat{r}'(\omega), \Delta \hat{r}''(\omega)$ sensibly different, in this range, from those given by setting κ_{q} to zero. Under this condition (1.21d) reduces to

$$\Delta f'_{q}(\omega) = \int_{\omega_{q}}^{\omega} \{\omega_{s}^{2}(dg/d\omega_{s})_{q}/(\omega^{2}-\omega_{s}^{2})\}d\omega_{s}$$
(1.21h)

and (1.21e) vanishes. However this does not mean that the imaginary part of (1.21) vanishes for note that the integrand in (1.21h) has a pole at $\omega = \omega_s$; but the integrand is well behaved either side of the pole so that the integration may be made along a contour on a complex plane as[†]

$$\left[\Delta f'_{q}(\omega)\right]_{\kappa_{q} \to 0} = P \int_{\substack{\omega_{q} \\ \omega_{q}}} \{\omega_{s}^{2}(dg/d\omega_{s})_{q}/(\omega^{2}-\omega_{s}^{2})\}d\omega_{s} + i(\pi/2)\omega(dg/d\omega_{s})_{q} (1.21i)$$
$$= \Delta f'_{q}(\omega) + i\Delta f''_{q}(\omega)$$
(1.21j)

where

$$\Delta f'_{q}(\omega) = P \int_{\omega_{q}} \{\omega_{s}^{2}(dg/d\omega_{s})/(\omega^{2}-\omega_{s}^{2})\}d\omega_{s}$$
(1.21k)

and $\Delta f_q''(\omega) = (\pi/2)\omega (dg/d\omega_s)_q$ (1.21*l*) whence it is seen that, though (1.21*e*) vanished, an imaginary term exactly

t like (1.21 g) is recovered; this is required for internal consistency to prevent a discontinuity in the imaginary term as $\kappa_{q} \rightarrow 0$.

⁺ The P in (1.21i) denotes that the principal part of the integral is to be taken, in this case, as $\lim_{\varepsilon \to 0} \left[\int_{\omega}^{\omega^2} \left(\frac{dg}{d\omega_s} \right)_q / \left(\frac{\omega^2 - \omega_s^2}{s} \right) d\omega_s + \int_{\varepsilon}^{\omega^2} \left(\frac{dg}{d\omega_s} \right)_q / \left(\frac{\omega^2 - \omega_s^2}{s} \right) d\omega_s \right]$ and this is finite.

[‡] Note that the standard text, Ref. 21 , is formally incorrect (at its Expressions 4.43, 4.43a, p.149 to give Expressions (1.21d) and (1.21e) above as mutually consistent results for $\Delta f'_q$ and $\Delta f''_q$. Literal evaluation of these results is overestimation of $\Delta f''_q$ by exactly factor 2 can be seen from (1.21i) above. The error arises when Ref. 21 sets κ_q to zero in its Expression (1.21d) and retains non-zero κ_q in its exposition of (1.21e). This is internally inconsistent since both expressions are devolved from the single expression (1.19) in which κ_q appears only once and the constant must be at least single valued. The error in Ref.21 is removed if only the principal part of the integral is included in its Expression 4.43 and its result 4.43 is regarded as originating in the residual of the integral and not in the manner given by Ref. 21 as its Expression 4.40.

Next, if the excitation energies for L-shell electrons of an irradiated atom are very far below the range of incident radiation energies then $\Delta f_{L}^{\,\prime}(\omega)$, $\Delta f_{I}'(\omega)$ may be safely set to zero for all these so that only K-shell electrons need be considered. For low Z elements the contributions ${}^{\Delta f}{}^{\prime}_{K}(\omega)$ and ${}^{\Delta f}{}^{\prime\prime}_{K}(\omega)$ are not negligible but they are still only minor contributions to fj. Therefore a first order approximation for them will leave negligible residual error in f_j (ω). Thus, all that is now needed for results is insertion of a reasonable approximation of $(dg/d\omega_s)_{F}$ in (1.21k), (1.21l) for the K electrons for $\omega \ge 2\omega_{c}$, followed by the summations (1.21b), (1.21) and (1.20). For these K-electrons it can be argued that hydrogenic wavefunctions are a good approximation and in those cases where, as above the anomalous terms are not large, we can expect negligible residual errors in f_j from use of it. This approach has the advantage that $(dg/d_{\omega_{S}})$ can be found analytically and s $\Delta f''_{\nu}(\omega)$ may also be found analytically. Hönl hence $\Delta f'_{\kappa}(\omega)$ and modifed Sigiura's³³ hydrogenic analysis by modelling the field in which each K-electron exists as of central form due to the nuclear charge moderated by a screening term due to the other K-electron and adding a constant potential term to allow for the effects of the outer orbitals. Hönl's $result^{34}$ is given by Ref. 21 as

 $(dg/d\omega_{s})_{K} = (2^{8}e^{-4}/9\omega_{K}) \{ [4/(1-\delta_{K})^{2}] (\omega_{K}/\omega)^{3} - [1/(1-\delta_{K})^{3}] (\omega_{K}/\omega)^{4} \} (1.21m)$ where $\delta_{K} = (A - 911/\lambda_{K})/A;$

It should be noted that the calculation above applies to favourable cases. 35 In any situation where any absorption edge of a constituent element occurs within (or even near to) the wavelength range of use of an analyser, or where an absorption edge other than a K-edge is significant, some of the approximations used above may not be adequate and other methods of evaluating (1.21d), (1.21e) will be needed.

<u>ii. Semi-empirical approach</u> The oscillator density function $(dg/dw_s)_q$ may be evaluated by relating it to an empirically determined quantity. Referring to Sections 1.5 and 1.6, the fractional amplitude scattered by a plane of unit cells is

$$q = i \operatorname{Nd}(\lambda/\sin\theta) F(\theta_{e},k) (e^{2}/mc^{2})p \qquad (1.22)$$

where θ is the glancing angle, θ_s is the direction of scattering with respect to the incident beam and P is the polarisation coefficient. Any imaginary term in $F(\theta_s, k)$ i.e a $\Delta f''(\omega)$ term, results in a corresponding term in q i.e. $\Delta q''$, being π out of phase with the incident beam, so that in the forward direction the resultant fractional amplitude is $(1 - \Delta q'')$. Thus the fractional loss in amplitude per plane traversed is

$$\Delta q'' = Nd(e^2/mc^2)(\lambda/\sin\theta) \sum_{j} \sum_{q} \Delta f''_{q}(\omega)$$
(1.23)

and the fractional loss in intensity per unit distance traversed is

$$2(e^{2}/mc^{2}) N \lambda \sum_{j q} \sum_{q} \Delta f''_{q}(\omega) = N \sum_{j q} \sum_{q} \mu_{q}(\omega) = \mu_{\ell}(\omega)$$
(1.24)

where μ_{ℓ} is the linear absorption coefficient of the material. Combination of (1.21g) and (1.24) gives

$$(dg/d\omega_s)_q = (mc/2\pi^2 e^2) \mu_q(\omega_s)$$
 (1.25)

where μ_q is the atomic photoelectron absorption coefficient (or photoelectric cross section) of q-types electrons at angular frequency ω_s . Appeal may now be made to measured data. Extensive absorption coefficient measurements show the following empirical relationship

$$\mu_{q}(\omega_{s}) = (\omega_{s}/\omega_{q})^{-P} \mu_{q}(\omega_{q}), \qquad \omega_{s} \ge \omega_{q}$$

$$= 0 \qquad , \qquad \omega_{s} \le \omega_{q} \qquad (1.26)$$

where ω_q is taken as the frequency for excitation to zero energy, i.e. excitations to bound states are neglected. This neglect is not generally justified and can result in serious errors in crystal parameter calculations at wavelengths within a few per cent of an absorption edge of a constituent atom. Furthermore for some orbitals, particularly the outer orbitals of high Z elements, the form of (1.26) is a poor approximation in general.

In circumstances to which (1.26) applies, provided measured values of $\mu_q(\omega_q)$ and p_q are available, then $\Delta f'(\omega)$, $\Delta f''_q(\omega)$ may be found by numerical integration of Expressions (1.21d) and (1.21e). Unfortunately it is difficult to measure $\mu_q(\omega_q)$ accurately especially for low energy absorptions in high Z elements. Alternatively there is resort to calculation of $\mu_q(\omega_s)$ from wavefunctions, a method which avoids the shortcomings of (1.26). However, in cases where (1.26) is applicable the calculation may be simplified by assuming the functional form of (1.26) so that the wave mechanical calculation is required at one frequency only. A literature search reveals the required wave mechanical results, though in a slightly different form. Putting (1.26) into (1.25) and the latter into a particular q-term in (1.19) results in

$$f_{q}(\omega) = g_{q}^{2\alpha}(\omega/\omega_{q})^{2}\omega_{q}^{pq^{+1}} \int_{\omega_{q}}^{\infty} [\omega_{s}^{-Pq}/(\omega^{2}-\omega_{s}^{2}-i\kappa_{q}\omega)]d\omega_{s}$$
(1.27)

where

œ

$$g_{q} = \int_{\omega_{q}} (dg/d\omega_{s})_{q} d\omega_{s} = (mc/2\pi^{2}e^{2})[\omega_{q}/(p_{q}-1)]\mu(\omega_{q})$$
(1.27a)

Therefore assuming the functional form of (1.26) calculation of the oscillator strength of g_q is equivalent to calculation of $\mu(\omega_q)$. In view of the availability of the Thomas-Reiche-Kuhn sum rule, g_q^{36} g_q rather than $\mu(\omega_q)$ is normally calculated. The lengthy procedure of numerical integration of Expressions (1. 21d) and (1. 21e) may be avoided by using Parratt and Hempstead's³⁷ evaluation of (1. 27) which is given by[†] $f_q(\omega) = g_q z(\omega/\omega_q)^2 \{1 - (\pi \alpha z^{\alpha} \gamma^{-n/2} / \sin \pi \alpha) + \alpha z^{\alpha} \sum_{k=0}^{m-1} \gamma^{kn} ln(1 - \gamma^{k} z^{1/m})\} (1.27b)$ $f_q(\omega) = g_q z(\omega/\omega_q)^2 \{1 + \alpha z^{\alpha} \sum_{k=0}^{m-1} \gamma^{k(m-n)} ln(1 - \gamma^k z^{-1/m})\} (1.27c)$ k = 0 when $|z| \ge 1$ where $0 < \alpha \equiv n/m \equiv \frac{1}{2} (p_q - 1) < 1, z \equiv (1 + in_q) / [(\omega/\omega_q)(1 + n_q^2)], n_q = \kappa_q / \omega$ and $\gamma = e^{-2\pi i / m}$ Expressions (1. 27b), (1. 27c) are the closed forms of Parratt and Hempstead's result, obtained when α is rational i.e. n and m are integers. Furthermore a particular value of α (or p_q) is assigned to a given $\frac{36}{7} 38$ orbital.

Evaluation of (1.27b), (1.27c) for each orbital in the atom j, followed by summation in (1.20) results in values of $f_j(\omega)$ which, from (I.21) and (1.21b), may be written as

$$f_{j}(\omega) = Z + \Delta f'_{j}(\omega) + i \Delta f''_{j}(\omega)$$
(1.28)

where each of the terms is a summation of dipole terms since Expression (1.19) was written for a set of dipole oscillators. The dipole approximation is appropriate for the anomalous dispersion terms but not in general for the normal dispersion term and therefore it is necessary to replace Z by the Hartree-Fock value of f_{0j} . Application of the Parratt and Hempstead method to crystal calculations are outlined in Refs.³⁹ and 40.

iii. Full wave mechanical treatment The hydrogenic wavefunction assumption and the power law derivation of $(dg/dw_s)_q$ are inadequate for the calculation of $\Delta f'(\omega)$, $\Delta f''(\omega)$ terms for heavy atoms for these approximations

The simple results for $\kappa_q = 0$ discussed in Subsection 1.2.c.i is in very close agreement with that of Parratt and Hempstead's for all values of ω to within less than 1% of ω_q for any plausible value of κ_q . Expression (1.26) is often a poor approximation that close to the edge so that there is doubtful need to retain $\kappa_q \neq 0$ and therefore doubtful need to prefer (1.27b), (1.27c) to the simpler expressions of James.

do not apply to the outer orbitals of such atoms. A more rigorous method is required and this may be found in the wave mechanical approach which derives expressions identical in form to (1.21d), (1.21e) giving the oscillator density as the co-ordinate matrix element

$$(dg/d\omega_{s})_{q} = (2m/3\hbar)\omega_{kn} \left| \int \psi_{k}^{*} \cdot \underline{\mathbf{r}} \cdot \psi_{n} d\underline{\mathbf{r}} \right|^{2}$$
(1.29)

where ψ_{k} is the co-ordinate wavefunction for a q-type electron in its rest that for the electron in the state to which the incident radiation state, Ψ'n first momentarily excites it, ω_{kn} is the angular frequency corresponding to the transition $k \rightarrow n$, \hbar is Planck's constant divided by 2π and the integration is made over all space. The function (1.29) must be evaluated for sufficient values of ω_{kn} to allow integration of Expressions (1.21d), (1.21e) to adequate precision. Expression (1.211) is based on approximation sufficiently good to allow its use in the determination of $\Delta f''(\omega)$ thus necessitating evaluation of (1.29) at the excitation frequency only but for evaluation of $\Delta f'(\omega)$ an integration over the frequency function of (1.29) is still required. For photon energies slightly less than the binding energy of q-type electron, (1.29), and consequently (1.21), can be expected to be rapidly varying functions for the cases of those orbitals which are easily excited to unoccupied bound states. If these excitations to bound states are neglected and the integrands in (1.21d), (1.21e) only allow for excitations to the positive energy continuum, then those integrands are much more slowly varying functions and may thus be defined for few evaluations of (1.29) so reducing the labour for determination of $\Delta f'_{q}(\omega)$ and $\Delta f''_{q}(\omega)$. In consequence there is considerable loss of accuracy in those results for excitation frequencies near those corresponding to excitation to bound states but little loss of accuracy for other photon energies. This approximation is incorporated in Expressions (1.21d), (1.21e) by integration over ω_q to ∞

rather than 0 to ∞ as is more properly the case. Cromer and Liberman calculate the photoelectric cross section as (1.29) for each orbital of each atom for five values of $\omega_{\rm KR}$ selected by the Gauss-Legendre integration method. Interpolation through the five values gives the form of the cross section versus ω curve and (1.21d) is applied to this form whereupon after a 5-point Gauss-Legendre integration, $\Delta f'(\omega)$ is obtained. The value of (1.29) is also required for the incident beam frequency in order to evaluate (1.21g). The value of (1.29) at these frequencies can be found by adaptation of Cromer and Liberman's method so as to interpolate the required values from the 5 tabulated values, somewhat assisted by the 5 additional values they list for the standard crystallographic frequencies. An example of the adoption of Cromer and Liberman's calculations in the determination of Bragg reflection properties for a heavy atom crystal is given in Ref. 43.

1.4 Unit Cell Scattering

Each atom in a unit cell scatters a wave of amplitude $f_j(\theta_s,k)$ and phase ϕ_j . Such a wave may be represented by a vector on an Argand diagram as shown in Fig.1.4 and the wave may be expressed as $f_j(\theta_s,k)e^{i\phi_j}$. The composite wave scattered by the N atoms in the unit cell is given by the resultant F which is the sum of the atomic vectors. The quantity F is the unit cell scattering factor (also known as the crystal structure factor) which

Cromer and Liberman develop their dispersion results from relativistic quantum theory of scattering. They retain the relativistic formulation for the major terms contributing to $\Delta f'$ and $\Delta f''$ and use a non-relativistic approximation for the minor terms. The cross sections like (1.29) they evaluated from the Brysk and Zerby⁴² relativistic photoelectric cross section program using Dirac-Kohn-Sham relativistic wavefunctions in the program. They restricted their calculations to dipole terms, neglected excitations to bound states and also neglected damping. For further details of their calculations Ref. 41 should be consulted.


Figure 1.4 An Argand diagram representation of the amplitude f and phase ϕ of a wave scattered by an atom in a unit cell



Figure 1.5 A two dimensional unit cell containing an atom with fractional co-ordinates x and y. The reflecting planes hk are also shown

may be written as

$$F(\theta_{s},k) = \sum_{j=1}^{N} f_{j}(\theta_{s},k) \exp(i\phi_{j})$$
(1.30)

An expression for ϕ_j suitable for computation may be derived with the aid of Fig.1.5 which shows a two dimensional unit cell containing an atom having fractional co-ordinates x and y. The hk reflecting planes are represented by a series of lines which cut the a axis in h parts and the b axis in k parts. Adjacent lines scatter with a phase shift of 2π so that a translation of a/h parallel to the a axis corresponds to a phase shift of 2π . If the scattering atom is first considered to be at the origin 0 where the phase value may be regarded as zero then a translation xa parallel to the a axis produces a phase shift ϕ_a given by

$$\phi_a/2\pi = xa/(a/h) = hx$$
 (1.31a)

and similarly a translation yb parallel to the b axis produces a phase shift $\ensuremath{^{\varphi}_{\rm b}}$ given by

$$\phi_{\rm b}/2\pi = yb/(b/k) = ky$$
 (1.31b)

The total phase shift of the scattering atom for the three dimensional case is thus

$$\phi = \phi_a + \phi_b + \phi_c = 2\pi (hx + ky + \ell z)$$
(1.32)

and substitution into Eqn. (1.30) gives

$$F(\theta_{s},k) = \sum_{j=1}^{N} f_{j}(\theta_{s},k) \exp[2\pi i(hx_{j} + ky_{j} + \ell z_{j})]$$
(1.33)

It is appropriate at this point to introduce a temperature factor

$$\begin{split} \exp(-T_{hk\ell}) & \text{which takes account of the diminution of the crystal structure} \\ \text{factor due to thermal vibration of the crystal atoms. Expression (1.33)} \\ \text{becomes} \quad F(\theta_s, k) = \sum_{j=1}^{N} f_j(\theta_s, k) \exp(-T_{hk\ell}) \exp[2\pi i (hx_j + ky_j + \ell z_j)] \quad (1.34) \\ \text{The inclusion of temperature effects will be discussed further in Section 1.7.} \end{split}$$

1.5 Scattering from a Plane of Unit Cells

The amplitude of a wave reflected by a plane of unit cells may be determined by the Fresnel zone treatment. In Fig 1.6 point S is the source of radiation and the amplitude of the reflected wave is required at point 0. The point P is such that SPO is the shortest distance from S to 0 via the plane. M is a point on the plane such that SMO is greater than SPO by $\lambda/2$ and thus the locus of the point M is the boundary of the first Fresnel zone the area of which is

$$(\pi r_1 r_2 / (r_1 + r_2)) (\lambda / \sin \theta)$$
 (1.35)

where r_1 and r_2 are the distances SP and OP respectively. The whole plane may thus be divided into successive Fresnel zones. The Fresnel zone treatment, which normally deals with a wavefront containing the sources of a large number of Huygen wavelets, is applicable because each zone contains a large number of unit cells so that a continuous distribution of scattering points can be assumed. The Fresnel construction shows that the resultant amplitude for the whole plane is half that due to the unit cells lying within the first Fresnel zone and the resultant amplitude due to the first zone is $2/\pi$ times the sum of the amplitudes due to the individual unit cells. Furthermore the phase of the wave at O is $\pi/2$ behind that of a wave scattered at P. It may be shown²¹ using Eqns.(1.6), (1.35) that, q, the ratio of the scattered amplitude to the incident amplitude is given by

$$q = -\frac{1}{2} \frac{\pi r_1 r_2}{r_1 + r_2} \frac{\lambda}{\sin \theta} - \frac{nF(\theta_s, k)e^2}{mc^2 r_2} p \frac{2}{\pi}$$
(1.36)

where p the polarisation coefficient is defined in the footnote on page 9 and n is the number of unit cells per unit area. The phase lag may be allowed for by expressing q, the reflection coefficient in the form -iq, since $e^{-i\pi/2} = -i$. It is more convenient to express n in the form n = Nd, where N is the number of unit cells per unit volume and d is the crystal planar spacing. Given that the incident wave is plane or nearly so, such that $r_1 > > r_2$,



Figure 1.6 Scattering from a plane of unit cells - the Fresnel zone construction



Figure 1.7 Scattering from a number of planes





the reflection coefficient of a plane of unit cells may be expressed as

$$- iq = + iNd(\lambda/sin\theta) F(\theta_{s},k)p(e^{2}/mc^{2})$$
(1.37)

1.6 Bragg Reflection by Idealised Crystal Structures

The theory of Bragg reflection is well defined for the cases of two idealised crystal models: the ideally perfect crystal and the ideally imperfect crystal. These two models, which are defined more fully below, lend themselves to two reflection theories: the ideally imperfect model to the kinematical theory and the ideally perfect model to the dynamical theory. The suitability of the theories to the appropriate models will become apparent from the following outlines of the theories.

1.6.1 The kinematical theory - the zero-extinction limit

The reflection of X-rays by a thin crystal may be described in terms of the kinematical theory which is based on the following assumptions:

a. the intensity of the incident beam is uniform throughout the crystal.

b. the interaction of the incident and scattered waves is negligible. Assumption a is valid, for since the crystal is thin, there is little loss of intensity due to absorption as the incident beam passes through the crystal. Also if the crystal were thick the upper planes of the crystal would reflect the incident beam and thus the intensity of the beam incident on the lower planes would be greatly diminished. Darwin⁴⁴ called this phenomenon primary extinction.

In assessing the validity of assumption b it is necessary to understand how the scattered beam may interact with the incident beam. Since the crystal planes are parallel, the wave reflected from a given plane can be reflected again by the plane above and this twice=reflected beam will be in the same direction as the incident beam. The magnitude of the twice-reflected beam from a single plane is negligible; therefore the effect is only of importance when it accumulates over a large number of planes and so may be neglected for a thin crystal.

Consider a thin crystal made up of n planes of spacing d which reflects a σ -polarised beam at glancing angle θ (see Fig.1.7). The region of the crystal which contributes to the scattered radiation at point Q is a cylinder having Q PP'P'' ... as axis and a diameter a few times that of the first Fresnel zone. The phase difference between the waves scattered by successive planes is $4\pi d(\sin\theta)/\lambda$. The resultant amplitude at Q is only significant in the region of the Bragg angle θ_B^{\dagger} at which angle the phase difference is an integral number times 2π and thus effectively zero. For the Bragg region let $\theta = \theta_B + \beta$ where β is small so that the phase difference is given by $\delta = 4\pi d \beta (\cos \theta_B)/\lambda$. On the basis of the kinematical theory the resultant amplitude A is given by

$$A/A_{o} = q\{1 + e^{i\delta} + \dots e^{-(n-1)i\delta}\} = q(1 - e^{in\delta})/(1 - e^{-i\delta})$$
 (1.38)

where A_0 is the amplitude of the incident radiation and q, the scattering amplitude of a single plane, is given by (1.37). The reflection coefficient i.e. the ratio of the intensities of the reflected and incident beams is obtained by multiplying (1.38) by its complex conjugate to give

$$P(\beta) = |q|^{2} [\sin^{2}(nB\beta)] / [\sin^{2}(B\beta)]$$
(1.39)

where $B=2\pi d(\cos\theta_B)/\lambda$. Expression (1.39) is of the same form as that of a diffraction grating of n elements and thus for large n, P(β) has a small but finite width. In fact P(β) is an example of a crystal diffraction function or crystal line spread function the definition of which is given in experimental terms in Chapter 2. Bragg⁴⁵ pointed out that the integral of this

⁺ This is the Bragg angle calculated from the simple Bragg law as given by Eqn. (1.5)

function is a measure of a crystal's 'intensity of reflection'. This integral is called the Bragg reflection integral and is denoted by R_c . It may be expressed in terms of experimentally measurable quantities by considering the ideal Bragg experiment (see Chapter 2) in which the crystal is scanned at an angular velocity ω , the incident beam has a cross sectional area S and the beam intensity, i.e. the energy passing per unit area in unit time, is $I'_o \cdot$ If it takes a time $d\beta/\omega$ to rotate the crystal through the small angular range $d\beta$ and the reflected beam intensity throughout this range is $I'_o^P(\beta)$ then E the total energy reflected in the Bragg reflection range is given by

 $E = I'_{o} S \int P(\beta) d\beta/\omega \text{ or } E\omega/I'_{o} = S \int P(\beta) d\beta = SR_{c}$ (1.40) Substitution of (1.37), (1.39) into (1.40) following the procedure of Ref.21, p. ³⁹ gives

 $E\omega/I_{O}' = (N^{2}\lambda^{3}/\sin 2\theta_{B})|F(2\theta_{B},k)|^{2} p^{2}(e^{2}/mc^{2})^{2} (ndS/\sin\theta_{B}) (1.41)$ The factor $ndS/\sin\theta_{B}$ is the volume of the crystal that is intercepted by the cylinder which has base area S and an axis that lies along the direction of reflection. Denoting this volume by Δv , (1.41) becomes $E\omega/I_{O}' = Q\Delta v$ where $Q = (N^{2}\lambda^{3}/\sin 2\theta_{B})|F(2\theta_{B},k)|^{2} p^{2}(e^{2}/mc^{2})^{2} (1.42)$

Equation (1.42) states that the total energy E reflected by a crystal that is sufficiently small for absorption to be neglected is proportional to the crystal volume and is independent of the crystal shape.

The following discussion shows that Eqn.(1.42) is also applicable to large real crystals. The diffraction profiles of such crystals are usually considerably broader than is predicted by Eqn.(1.39) indicating the presence of imperfections in these crystals. Darwin suggested that the imperfections were due either to warping in the atom planes or to cracking. The latter suggestion led him to propose that most crystals are made up of small blocks (or domains), each block being a perfect crystal. The atomic planes of separate blocks are nearly parallel such that all the blocks are distributed in orientation over an angular range which, although small, is greater than the width of the response function of a single block. Ewald later called this model the 'mosaic' crystal model. Darwin adopted the mosaic crystal model rather than the model based on atomic plane warping because mathematically it was easier to handle. Later experimental evidence shows in fact that most crystal imperfections are due to mosaic structure rather than warping. Nevertheless the mosaic model is an oversimplification since imperfections in crystals are caused by dislocations, strains, intersticial atoms, etc., rather than by the crystal being simply divided into discrete blocks.

The diffraction profile characteristics of a mosaic crystal depend upon the size of the blocks and the distribution function of the block orientations. Clearly if this distribution function is broad so the diffraction profile of the crystal is also broad. If the blocks are large then there are integrated intensity losses due to primary extinction which is discussed above. If the block orientation distribution function is narrow, it is highly probable that a block in the crystal interior which is orientated to reflect, will receive an incident beam of diminished intensity since a similarly orientated block nearer the surface will reflect the beam. Darwin called this effect secondary extinction. Clearly extinction is small and accordingly the Bragg reflection integral is high, when the crystal domains are small and their orientation distribution function is broad. The limiting case of zero extinction, often referred to as the ideally mosaic or ideally imperfect model, provides a useful model for calculating the reflection integral of an imperfect crystal. Although few crystals are ideally imperfect a comparison of measured reflection integral values with those calculated from the Darwin zero-extinction limit gives a measure of the degree of imperfection of real crystals. Some

crystals can be made to approach the ideally imperfect state by undergoing various treatments as described in Chapter 4.

Since the crystal domains of an ideally mosaic crystal are optically independent i.e. reflections from different blocks are incoherent with respect to each other, the total intensity reflected by the crystal is simply the sum of the intensities reflected by the individual blocks. Figure 1.8 shows a mosaic crystal in which a block of volume dv, lying at a depth z below the crystal surface, is irradiated by a beam of cross sectional area S₀ and intensity I'₀. The radiation reflected by this block travels a distance $2z \operatorname{cosec} \theta_{B}$ through the crystal and therefore is reduced in intensity by a factor $e^{-2\mu_{R}z\operatorname{cosec}\theta_{B}}$ where

 μ_{g} is the linear absorption coefficient. If dE is the contribution of this block to the total energy E reflected on rocking the crystal at an angular velocity ω through the angular range of reflection, then by Eqn (1.42)

$$\omega dE/I'_{O} = Q e^{-2\mu_{\ell} z cosec\theta_{B}} dv$$
(1.43)

The total energy reflected by the crystal is obtained by integrating (1.43)over the volume of crystal that is irradiated. Noting that the volume of the small block is $S_0 \cos \varepsilon \theta_B dz$ this integration yields

$$E\omega/I_{o}' = Q \int_{o}^{\infty} e^{-2\mu_{\ell}z \operatorname{cosec}\theta} B \operatorname{cosec}_{B} dz = Q S_{o}/2\mu_{\ell}$$
(1.44)

or

$$E\omega/I_{o} = R_{c} = Q/2\mu_{l}$$
 (1.45)

where $I_0 = I_0^{\prime} S_0^{\prime}$ is the total energy per unit time incident on the crystal. Substituting for Q from Eqn.(1.42) the Bragg reflection integral for the Darwin zero-extinction limit is

$$R_{c} = (N^{2}\lambda^{3}/\sin 2\theta_{B}) |F(2\theta_{B},k)|^{2} (p^{2}/2\mu_{l}) (e^{2}/mc^{2})^{2}$$
(1.46)

Since the reflection integral for unpolarised radiation is the mean of those for the σ - and π - polarised cases, then for an unpolarised beam

$$R_{c} = (N^{2}\lambda^{3}/\sin 2\theta_{B}) |F(2\theta_{B},k)|^{2} [(1 + \cos^{2}2\theta)/4\mu_{\ell}] (e^{2}/mc^{2})^{2} (1.47)$$

Equations corresponding to (1.47) may be obtained for the Bragg reflection integral of the Darwin zero-absorption limit and the Prins perfect lattice limit both of which are discussed in Subsection 1.6.1.

1.6.1 The dynamical theory

The dynamical theory of X-ray reflection provides a theoretical framework for describing Bragg reflection by perfect crystals. The theory is based on the assumption that the interaction between incident and scattered radiation inside the crystal medium is non-negligible. In 1914, only two years after the discovery of X-ray diffraction, Darwin²⁰ proposed the first dynamical theory of X-ray diffraction. Soon afterwards Ewald⁴⁶ independently presented a treatment which involved regarding the crystal as a lattice array of electric dipoles and considering a dynamic equilibrium between the wave-field within the crystal and the dipole oscillations. In 1931 Laue⁴⁷ developed Ewald's treatment and expressed the theory in terms of the solution of the Maxwell equations for a medium with a periodic complex dielectric constant. The Darwin treatment, although less general and elegant than the Ewald-von Laue treatment, gives a more straightforward account of X-ray diffraction by perfect crystals and so this approach is adopted below. Full accounts of the Ewald-von Laue treatment are given in Refs. 48, 49, 21 and 50.

a. Reflection by a perfect crystal with negligible absorption - the zeroabsorption limit

Darwin's formulation of the dynamical theory involved considering X-ray reflection by a series of parallel planes as shown in Fig.1.9. Each plane is indexed by the value of r where r = 0 for the surface plane. The total incident and reflected waves at a point just above the rth plane are denoted by T_r and S_r respectively. The diffraction profile is obtained from S_0/T_0 the



Figure 1.9 Dynamical reflection from a set of parallel crystal planes



Figure 1.10 Darwin zero-absorption function



Figure 1.11 Prins perfect lattice function for pentaerythritol (002) at 8.34 ${\rm \AA}$

ratio of the reflected and incident waves at the crystal surface. Darwin calculated the ratio by setting up a pair of difference equations based on the following considerations which take account of the interaction between incident and reflected radiation in the crystal. S_r , for instance, is the sum of the reflected part of T_r and the transmitted part of S_{r+1} whilst T_{r+1} is the sum of the transmitted part of T_r and the part of S_{r+1} which is reflected from the lower side of the rth plane. The reflection coefficient - iq for a plane of unit cells is given by Eqn.(1.37). The amplitude $-iq_0$ of the forward scattered wave is obtained by calculating Eqn.(1.37) for $\theta_s = 0$. The amplitude of the incident beam after transmission is the resultant of the incident amplitude (of unit value) and the forward scattered amplitude i.e. 1 - iq_0 , and this is referred to as the transmission coefficient. The path difference for two successive planes is $d \sin \theta$ and therefore the value S_{r+1} just below the rth plane is $S_{r+1}e^{-i\phi}$, where $\phi = (2\pi/\lambda)d\sin\theta$. The following difference equations may now be constructed

- 1

$$S_{r} = -iqT_{r} + (1 - iq_{0})e^{-i\varphi}S_{r+1}$$
(1.48)

$$T_{r+1} = (1 - iq_0)e^{-i\phi}T_r - i\bar{q}e^{-2i\phi}S_{r+1}$$
(1.49)

where \bar{q} is the reflection coefficient of the lower side of the plane. It should be noted that \bar{q} differs from q for a polar crystal. Substitution for S_{r+1} in (1.48) by an expression derived from (1.49) and for S_r from a corresponding expression with r diminished by one, gives

$$(1 - iq_0)(T_{r-1} + T_{r+1}) = \{q\bar{q}e^{-i\phi} + (1 - iq_0)^2 e^{-i\phi} + e^{i\phi}\}T_r (1.50)$$

A trial solution of Eqns.(1.48), (1.49) and (1.50) is given by

$$T_{r+1} = x T_n$$
 (1.51)

where x is independent of r. Substitution of (1.51) in (1.50) gives the following

$$(1 - iq_0)((1/x) + x) = q\bar{q}e^{-i\phi} + (1 - iq_0)^2 e^{-i\phi} + e^{i\phi}$$
(1.52)

Apart from the phase factor the value of T changes little for successive planes.

Since only values of θ near the Bragg angle θ_B are important the value of the phase factor is nearly equal to $m\pi$. From these considerations x may be expressed as

$$x = (1 - \xi)e^{-im\pi}$$
 (1.53)

where ξ is small and may be complex. It is convenient to introduce a quantity v given by

$$\phi = m\pi + v , \qquad (1.54)$$

$$v = 0 \text{ when } \theta = \theta_{p} .$$

Substituting from (1.53) and (1.54) into (1.52), expanding, and neglecting

terms of powers higher than two, yields

$$\xi^{2} = q\bar{q} - (q_{0} + v)^{2}$$
(1.55)

Now substitution of (1.51) into (1.48) and (1.49) gives $S_{r+1} = xS_r$ and substitution of this into (1.48) putting r = 0 gives

$$S_0/T_0 = -iq/[1 - x(1 - iq_0)e^{-i\phi}]$$
 (1.56)

Substituting for x and ϕ expanding e^{-iv} and retaining only first powers of small quantities in the expansion of the denominator:

$$S_0/T_0 = -q/[q_0 + v \pm ((q_0 + v)^2 - q\bar{q})^{\frac{1}{2}}]$$
 (1.57)

In the case of zero absorption it is convenient to divide throughout by $(2\pi/\lambda)d\cos\theta_{\lambda}$ (where θ_{λ} is the Bragg angle corrected for the refractive index) and introduce the following quantities

$$\varepsilon = \theta - \theta_{1} = (q_{0} + v) / ((2\pi/\lambda)d \cos\theta_{1})$$
(1.58)

$$s = q/((2\pi/\lambda)d \cos\theta_{\lambda})$$
(1.59)

Noting that $q = \bar{q}$ for the case of zero absorption, (1.57) becomes

$$S_{o}^{T}/T_{o} = -s/[\epsilon \pm (\epsilon^{2} - s^{2})^{\frac{1}{2}}]$$
 (1.60)

The ambiguity of sign in the denominator is resolved by the condition that

 $S_0/T_0 < 1$. The ratio of the reflected and incident beam intensities at the surface is given by $I/I_0 = (S_0/T_0)(S_0/T_0)^*$ and for S_0/T_0 given by (1.60), I/I_0 as a function of ε is referred to as the Darwin zero-absorption response function $P(\varepsilon)$. The values of this function for the three principal

$$\varepsilon < -s , P(\varepsilon) = s^{2} / [\varepsilon - (\varepsilon^{2} - s^{2})^{\frac{1}{2}}]^{2}$$

- s < \varepsilon < + s , P(\varepsilon) = s^{2} / [\varepsilon^{2} + s^{2} - \varepsilon^{2}] = 1 (1.61)
\varepsilon > + s , P(\varepsilon) = s^{2} / [\varepsilon + (\varepsilon^{2} - s^{2})^{\frac{1}{2}}]^{2}

The function is distinctive in that it is flat topped and in the flat or middle region (-s < ε < +s) reflection is 100%. Figure 1.10 shows a plot of the Darwin zero-absorption response function in which the angular variable is ε/s . The function is symmetrical about the corrected Bragg angle θ_{λ} . The full width at half maximum w_c of the function is given by

$$W_{c} = 3s/2^{\frac{1}{2}}$$
 (1.62)

The integral of the Darwin zero-absorption response function is obtained by summing the integrals of the function for the three angular ranges considered above in Eqn.(1.61) thus

$$R_{c} = \int_{\epsilon=-\infty}^{-S} P(\epsilon)d\epsilon + \int_{\epsilon=-\infty}^{+S} P(\epsilon)d\epsilon + \int_{\epsilon=-\infty}^{\infty} P(\epsilon)d\epsilon \qquad (1.63)$$

= s/3 + 2s + s/3 = 8s/3 (1.64) Substituting for s from Eqns.(1.37), (1.59) and noting that for the small angular range of significant reflection θ_B, θ_λ are interchangeable, the integral of the Darwin zero-absorption response function is given by

$$R_{c} = (8/3\pi) (N\lambda^{2} \sin 2\theta_{B}) |F(2\theta_{B}, k)| p(e^{2}/mc^{2})$$
(1.65)

It should be noted that in (1.65) F ($2\theta_B, k$) does not include anomalous dispersion terms.

b. Reflection by a perfect crystal with absorption - the general (Prins) perfect lattice limit

Darwin attempted to take account of absorption of radiation due to the photoelectric effect and incoherent scattering by introducing an absorption factor h such that the transmission coefficient at each plane became $1-h-iq_0$. Later in his treatment of the dynamical theory Darwin ignored the factor h explaining that it was only introduced in the first instance to give validity to

the treatment. Prins⁵¹ allowed for absorption more satisfactorily by introducing a complex refractive index given by

$$n = 1 - \delta - i\beta \tag{1.66}$$

where δ and β are respectively the real and imaginary parts of the unit decrement of the refractive index.⁺ References 21 and 52 show that

$$\delta + i\beta = \sum_{j} (\delta_{j} + i\beta_{j}) = \sum_{j} (\lambda^{2}e^{2}/2\pi mc^{2})(1/V)f_{j}(0,k)$$
(1.67)

In this expression V, the volume of the unit cell, can be found from the expression V = $M/(\rho N_A)$ where ρ is the material density, M is the gram molecular weight and N_A is Avogadros number. From (1.67) it follows that

$$\delta = \sum_{j} \delta_{j} = \sum_{j} (e^{2}/mc^{2}) (1/2\pi) (1/V) \lambda^{2} (f_{0_{j}}(0,k) + \Delta f'_{j}(\omega))$$
(1.68)

$$\beta = \sum_{i}^{\beta} \beta_{j} = \sum_{i}^{\beta} (e^{2}/mc^{2}) (1/2\pi) (1/V) \lambda^{2} \Delta f_{j}^{"}(\omega)$$
(1.69)

In the Prins method δ and β are equated with q_0 by the following expression ‡

$$- (\delta + i\beta) = (\lambda/2\pi d) \sin\theta_{B} q_{O} \qquad (1.70)$$

The corresponding equations for q and \overline{q} are as follows

$$- (D_1 + iB_1) = (\lambda/2\pi d) \sin\theta_B q \qquad (1.71)$$

$$- (D_2 + iB_2) = (\lambda/2\pi d) \sin\theta_B \bar{q} \qquad (1.72)$$

where $D_{1,2}$ and $B_{1,2}$ the Prins (unit cell) parameters are given by $D_{1,2}^{+iB}_{1,2} = \sum_{j} [p(\delta+i\beta)_{j} \{ [f_{j}(2\theta_{B},k)/f_{j}(0,k)] \} exp(T_{hkl}) exp[+, -2\pi ni(hx_{j}^{+ky}_{j}^{+lz}_{j})]$ (1.73)

Substituting (1.70), (1.71) and (1.72) into (1.57) the ratio of the intensities of

the incident and reflected beams $P\left(\theta~-~\theta_{B}^{}\right)$ is given by

ŧ

In the Darwin method the refractive index is considered real so that $n=1-\delta=1-(\lambda/2\pi d)\sin\theta_Bq_o$.

30

It is easily shown as follows that a complex refractive index takes account of absorption. Consider a wave travelling in a direction x in a medium of refractive index n. The displacement at a point x is obtained by multiplying by the factor exp - i $(2\pi/\lambda)$ nx which for a complex refractive index may be written as $\exp-i(2\pi/\lambda)(1-\delta)x \exp-(2\pi/\lambda)\beta x$. Thus β the imaginary part of the refractive index is concerned with the diminution of the wave amplitude with increasing x which corresponds to absorption.

 $[\]beta$ may therefore be related to μ_{ℓ} , the linear absorption coefficient, thus $\beta = (\lambda/4\pi)\mu_{\ell}$ (1.66a) This relationship may be derived from comparison of Expressions (1.24), (1.69).

$$P(\theta - \theta_{B}) = [\{(D_{1} + iB_{1})\}/\{c \pm [c^{2} - (D_{1} + iB_{1})(D_{2} + iB_{2})]^{\frac{1}{2}}\}]^{2}$$
(1.74)
where $c = cos\theta_{B}sin\theta_{B}(\theta - \theta_{B}) - \delta - i\beta$

40

Expression (1.74) is known as the Prins response function for the perfect lattice limit or more generally as the Prins curve. The curve, as can be seen in Fig 1.11 is asymmetric due to absorption. It is roughly centred about the angle θ_{λ} given by

$$\theta_{\lambda} - \theta_{B} = \delta \sec \theta_{B} \csc \theta_{B}$$
(1.75)

The right hand side of (1.75) represents the correction to the Bragg angle due to the refractive index. It is convenient in calculation to adopt θ_{λ} as the origin for angular measurement and to introduce the angular variable λ defined by

$$\ell = (\theta - \theta_{\lambda}) / (\theta_{\lambda} - \theta_{B}) = \delta^{-1} (\theta - \theta_{B}) \sin \theta_{B} \cos \theta_{B} - 1$$
(1.76)

Eqn. (1.74) now becomes

 $P(\ell) = \left| \left((D_1 + iB_1) / \delta \right) / \left(\ell - i(\beta / \delta) \pm \left[\left[\ell - i(\beta / \delta) \right]^2 - \left[(D_1 + iB_1) (D_2 + iB_2) / \delta^2 \right] \right\}^{\frac{1}{2}} \right) \right|^2$ (1.77) which is the form of the Prins function given in Ref. 52. The integral of the function will be discussed in Subsection 1.8.c.

1.7 Inclusion of Temperature Effects

The thermal energy of crystal atoms causes them to vibrate about their mean position and consequently the in-phase scattering expected from a plane of static atoms is destroyed to some extent. The amplitude of atomic scattering is reduced and this is taken into account theoretically by multiplying the atomic scattering factor f of a given atom by a temperature factor of the form $\exp-T_{hkl}$ such that

$$f_{T} = f_{R} \exp{-T_{hk\ell}}$$
(1.78)
where f_{T} is the atomic scattering factor at absolute temperature T and f_{R}
is the atomic scattering factor when the atom is at rest. Debve⁵³ presented

the first extensive treatment of temperature effects in which he considered that each atom vibrated independently and that atomic energies were governed by Boltzmann statistics. Clearly, on account of interatomic forces, the assumption of independent vibrations was unreasonable and so using a method presented by Born and Karman⁵⁴, Debye recalculated his results to include interatomic forces and thus obtained the following expression for the exponent of Eqn. (1.78)

$$M = (3h^2/m_a k\Theta) [(\Phi(x)/x) + (1/4)] (\sin^2\theta/\lambda^2)$$
(1.79)

where h is Planck's constant, m_a is the atomic mass, k is the Boltzmann constant, $x = \Theta/T$, where Θ is the characteristic temperature of the crystal and $\Phi(x)$ is a function of x, values of which are given in Debye's paper and Ref. 52. Debye's treatment applied to crystals with only one atomic species so that the total correction for temperature effects is simply obtained by multiplying the crystal structure factor by exp - M. Waller⁵⁵ reassessed Debye's treatment to find that Debye's temperature factor was too small by a factor of two and so he introduced the temperature factor exp - 2M, later to be known as the Debye-Waller factor, where M is given by Eqn. (1.79). Extensive discussions of the Debye-Waller factor are given in Refs. 21,52,56 49 and 57. Waller also extended Debye's treatment to deal with crystals of more than one atomic species. In general Debye-Waller temperature factors are not easily evaluated since they require knowledge of characteristic temperatures which may not be readily available. A more successful approach to temperature effects finds its roots in the work of Waller and James⁵⁸ who expressed the temperature factor as follows

$$\exp - (2\pi^2 < u^2)/d^2 = \exp - [8\pi^2 < u^2](\sin^2\theta)/\lambda^2$$
(1.80)

where $\langle u^2 \rangle$ is the mean square displacement of an atom from the reflecting

plane¹² In the last fifteen years it has been common practise in crystallographic literature to present, alongside atomic co-ordinate data, temperature parameters necessary to calculate the exponents in Expression (1.80). There are two types of temperature parameters and these are discussed below using the nomenclature of Ref.12.

Isotropic temperature parameters If the restoring forces acting upon a

vibrating atom are the same in all directions then the field of restoring forces is said to be isotropic. For such a field the temperature factor of an atom is expressed in terms of an isotropic temperature parameter B which is equal to

$$8\pi^2 < u^2 > .$$
 Thus
 $exp-T_{hkl} = exp-B(sin^2\theta)/\lambda^2$ (1.81)

The dimensions of B are in square Ångstroms. In crystallographic literature, values of B may be given for individual atoms or merely for atomic species. Quite often a parameter $U(= \langle u^2 \rangle)$ is presented from which B may be calculated.

Anisotropic temperature parameters The field of restoring forces in general varies with direction and is therefore described as anisotropic. The nature of such a field is taken into account by expressing the exponent of Expression (1.80) in terms of a six parameter tensor.^{59,60} This parameter is derived by expressing the left hand side of Expression (1.80) in terms of the reciprocal lattice vector so that

$$1/d^{2} = \left| r_{hkl}^{*} \right|^{2} = (ha^{*} + kb^{*} + lc^{*})(ha^{*} + kb^{*} + lc^{*})$$
$$= h^{2}a^{*2} + k^{2}b^{*2} + l^{2}c^{*2} + 2hka^{*} \cdot b^{*} + 2klb^{*} \cdot c^{*} + 2lhc^{*} \cdot a^{*}$$
(1.82)

Each of the terms in Eqn. (1.82) must be multiplied by its characteristic

and thus

$$exp-T_{hkl} = exp-2\pi^{2} (U_{11}h^{2}a^{*2} + U_{22}k^{2}b^{*2} + U_{33}l^{2}c^{2} + 2U_{12}hka^{*}b^{*} + 2U_{23}klb^{*}c^{*} + 2U_{31}lhc^{*}a^{*})$$
(1.84)
where $U_{12} = u_{12}\cos(a^{*}b^{*})$, etc.

Another common expression for the anisotropic temperature coefficient is given by

$$\exp - T_{hkl} = \exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{31}lh)$$
(1.85)

Values of the U and B parameter series are given in crystallographic literature.

The consequences of temperature effects with respect to the parameters of crystal response functions may be discerned from the Darwin zeroabsorption and Prins perfect lattice models. It is clear from Expressions (1.65) and (1.62) that for the Darwin model both R_c and w_c are reduced and indeed Batterman⁶¹ has observed reflection integral reduction and thermal narrowing in silicon crystals. It is worth noting that temperature effects increase rapidly with diffraction order and indeed it was found for the ADP calculations of this work that first order reflection integrals were reduced by

~ 1% whereas fourth order reflection integrals were reduced by ~ 20%. The Darwin model still predicts a region of total reflection but one which is reduced in range. In the case of the Prins perfect lattice model a reduction in $P(\ell)$ over the whole range of the function might be expected and indeed from calculations this is found to be the case.

1.8 Numerical Evaluation

Computer programs were written to calculate the functions derived from the idealised crystal models discussed in this chapter. General computational details are given below and further details are given in Appendix A. Details of data sources for a given crystal are included in the relevant crystal study chapter.

a. Darwin zero-extinction limit

Expression (1.46) was programmed to give an analytical calculation of R_c for σ,π polarised cases and the unpolarised (u) case. μ_{ℓ} was calculated from $\Delta f''$ terms using Expression (1.24). The value of μ_{ℓ} was outputted and compared with experimental values.⁶² The 2-reflection integral $R_{cc,u}$ was determined from $R_{c,u}$ using Expression (2.54) with polarisation factor k=cos²20. The above calculations are part of the EWALD program, an outline of which is given in Appendix A.

b. Darwin zero-absorption limit

i. Analytical computation The function and its integral were calculated from Expressions (1.61) and (1.65) respectively for σ and π polarisations. The value of the function for unpolarised radiation is, for a given point, the average of the σ and π values at that point. Similarly the reflection integral for unpolarised radiation is the average of the σ and π integrals. The width of the function for σ and π polarisations was calculated from Expression (1.62). Evaluation of the width for unpolarised radiation is outlined in Paragraph ii below.

The 2-crystal response function P (β) (where β is measured from the parallel position (see Section 2.3.3) for a given polarisation is obtained from the autocorrelation of P (ϵ), thus

$$P (\beta) = \int_{-\infty}^{\infty} P(\varepsilon)P(\varepsilon-\beta)d\varepsilon / \int_{-\infty}^{\infty} P(\varepsilon)d\varepsilon$$
(1.86)

Since P (ϵ) is symmetric it need only be evaluated for $\beta \ge 0$. It is convenient to evaluate (1.86) for two cases: Case 1 $\beta \le 2s$ and Case 2 $\beta \ge 2s$ where s is defined by Expression (1.59). It is convenient to break down (1.86) into a series of integrals⁶³ and for Case 1 it can be shown that

P (
$$\beta$$
) = 3/8s{2s - β + 2 $\int_{S}^{S+\beta} P(\varepsilon)d\varepsilon$ + 2 $\int_{S+\beta}^{\infty} P(\varepsilon)P(\varepsilon - \beta)d\varepsilon$ } (1.87)
A similar expression may be derived for Case 2. The first integral contains
the rapidly changing part of the Darwin function and can be evaluated by
integration of Expression (1.61) for ε > s to give

 $\int_{S} P(\varepsilon)d\varepsilon = \{(1/u_1)[(1/3u_1^2) - 1] - (1/u_2)[(1/3u_2^2) - 1]\}(1.88)$ $u_1 = s + \beta + \sqrt{(s+\beta)^2 - 1} , \quad u_2 = s + \sqrt{s^2 - 1}$

Evaluation of the second integral requires lengthy algebra. The integral may be expressed as a series of six integrals, five of which can be evaluated by means of hyperbolic or algebraic substitutions and the remaining integral can be evaluated using elliptical functions and integrals. Details and results of the algebraic manipulations are given in Ref 63. A similar procedure to that of Case 1 is required for Case 2.

The 2-reflection function widths for the σ and π polarisation are calculated from the expression $w_{cc}=1.32 w_c$ (Ref. 52, Eqn. 9.71) which is derived in Ref.63. The 2-reflection function width for the unpolarised case is evaluated numerically as described in the next paragraph. The 2-crystal reflection integral is calculated from Expression (2.54) using the polarisation factor $k = |\cos 2\theta|$.

ii. Numerical computation

Since the 1-reflection function and its integral are easily obtained analytically there was no need to proceed with numerical evaluation. The 2-reflection function can be determined numerically using Expression (1.87). The last integral of this expression and other integrals arising from Case 2 can be integrated using Simpson's rule. This integration method requires an odd number of points in the tail and flat regions of the Darwin function. The program achieves an odd number of points by calculating the half width of the flat region and then adjusting the inputted step length accordingly. As a result of this $P_{\sigma}(\beta)$ and $P_{\pi}(\beta)$ are evaluated at different points and so instead a mean value, $P_u(\beta)$ must be determined by interpolation. Some of the integrals involved have infinite limits and so it is necessary to integrate with finite limits and iterate until sufficient accuracy is achieved. The widths of $P_{\sigma}(\beta)$, $P_{\pi}(\beta)$, $P_{u}(\beta)$ as well as $P_{u}(\epsilon)$ are determined numerically by scanning the array holding the computed function to find the position which holds a value just less than half the maximum. Linear interpolation is then used to determine the width. All reflection integrals are calculated analytically. An outline of the program DARWIN, which calculates the Darwin zero-absorption function numerically and analytically is given in Appendix A. It should be noted that evaluation of $F(2 \theta_{B}, k)$ for the Darwin zero-absorption function excludes anomalous dispersion terms.

c. Prins perfect lattice limit

i. Analytical computation The Prins integral was calculated (see Appendix A, Program EWALD) using the analytical expression derived by Afanas'ev and Perstnev.⁶⁴ The elliptical integrals of their expression were calculated by a power series summation but where the series were slow to converge the approximations introduced by Afans'ev and Perstnev were applied. For full details Refs.63 and 64 should be consulted. The 2-reflection integral was calculated using Expression (2.50).

ii. Numerical computation The Prins function P(l) was generated by programming Expression (1.77). The σ and π values of the functions at a given point were averaged to give the value for unpolarised radiation.

The widths of $P(\ell)$ for the three polarisation cases were evaluated by determination of the half peak height value and linear interpolation between the points on either side of this value. The reflection integrals were calculated by numerical integral of the function using Simpson's rule. The 2-reflection function $P(\beta)$ (where β is the angular deviation from the central position) was generated by numerical convolution using Simpson's rule to calculate areas. The curve for the unpolarised case was generated as for the 1-reflection curve. The widths and integrals of $P(\beta)$ for the three polarisation cases were determined numerically as above. Details of numerical calculations for the Prins perfect lattice limit are given in the outline of Program PRINS in Appendix A.

CHAPTER 2 : PRINCIPLES OF THE MEASUREMENT PROCEDURES FOR CHARACTERISATION OF BRAGG ANALYSERS

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CHAPTER 2

PRINCIPLES OF THE MEASUREMENT PROCEDURES

FOR CHARACTERISATION OF BRAGG ANALYSERS

Introduction

Characterisation of the Bragg response for an analyser entails the determination, of the Bragg dispersion function, and of the line spread function, over the X-ray wavelength range spanning the short wavelength and 2d limits of the crystal. In order to proceed with an empirical evaluation of these functions, they must be defined with respect to experimentally measurable quantities.

The Bragg dispersion function

This function is essentially a form of the Bragg equation corrected for the characteristic dispersion of the Bragg analyser. It relates λ , the incident beam wavelength, d_T the lattice period at temperature T(^OC) and $\theta_{\lambda,n}$ the angle, at the position of the interference maximum, between the external incident ray and the diffracting plane of the crystal for the nth order. It may be expressed as

$$n\lambda = 2d_{T} \sin \theta_{\lambda,n}$$

$$= 2d_{T} \sin (\theta_{B} + \Delta \theta(\lambda,T))$$
(2.1)

where $d_{T} = d_{18} (1 + \alpha (T - 18))$ In these expressions $\theta_{\mathbf{B}}$ is the solution to the simple Bragg equation for wavelength λ , $\theta_{B} = \sin^{-1} (n_{\lambda}/2d_{T})$, α is the linear expansion coefficient in the direction normal to the diffracting planes and $\ \ \Delta\theta$ (λ , T) is the contribution to $\theta_{\lambda,n}$ arising from dispersion. Geometrical refraction theory, based upon Snell's Law, easily shows that 52 †

> $\Delta \theta = \delta \sec \theta \csc \theta$ (2.3)

+ Angles will be denoted by θ , in generic expressions, in cases where the approximation $\theta_{\lambda,n} \simeq \theta_{B}$ is valid and in cases where the distinction between $\theta_{\lambda,n}$ and θ_{B} is unimportant.

(2.2)

where δ is defined as the unit decrement of the refractive index and is calculated as Expression (1.68)

 $\delta = \sum_{j=1}^{\infty} \delta_{j} = \sum_{j=1}^{\infty} (e^2/mc^2) (1/2\pi) (1/V) \lambda^2 (f_{oj}(0,K) + \Delta f'_j(\omega))$ This expression clearly shows that $\Delta \theta$ is wavelength dependent. Noting that $f_{oj}(0,k)$ and $\Delta f'_j(\omega)$ are associated with normal and anomalous dispersion respectively then (2.3) can be expressed as

$$\Delta \theta = (\delta_{N} + \delta_{\Delta}) \quad \sec \theta \quad \csc \theta \tag{2.4}$$

where δ_N and δ_A are respectively the normal and anomalous dispersion contributions to δ . It should be noted that f_{0j} (O, k) and $\Delta f'$ are wavelength independent and wavelength dependent respectively. Note also that (1.68) reveals a temperature dependence in $\Delta \theta$ arising from the term in 1/V. However since it will be seen from later discussion that $\Delta \theta$ is a small quantity the temperature dependence of that small quantity arising from the expansion coefficient α (where α is of the order of 1 part in 10⁵ per Kelvin) will be negligible for the range of laboratory temperature of concern.

The required quantities for the complete description of the dispersion function are d₁₈, α and $\Delta \theta(\lambda)$.

The line spread function

It is observed and predicted from crystal diffraction theory that the Bragg reflection of an X-ray beam, of infinitesimal beamspread and of infinitesimal bandwidth, occurs over a small angular range as a result of the finite width of the crystal line spread function. In this small angular range the reflected beam intensity I is given by

$$I(\theta) = P_{1}(\theta) I_{0}$$
 (2.5)

where I_0 is the incident beam intensity, θ is the crystal aspect angle to the incident beam, λ is the wavelength of the incident beam and $P_{\lambda}(\theta)$ is the value of the line spread function at a given θ . The variation of $P_{\lambda}(\theta)$ with θ over

the angular range of significant reflection gives the profile of this function at wavelength λ . The function profile changes with wavelength hence crystal characterisation requires determination of the profile over the crystal wavelength range. This determination must for reasons given in the Introduction reveal the integral and shape of the profile.

The integral of the function may be defined with reference to an idealised experiment where the beam characteristics are as above. If the crystal aspect angle is changed at a constant rate $d\theta/dt = \omega$ then the total count, E, obtained in scanning a range of θ , which embraces the region of significant Bragg reflection, is

$$E = I_0 \int_{\theta_1}^{\theta_2} P_{\lambda}(\theta) d\theta / \omega$$
 (2.6)

Because this function tends to zero relatively quickly away from the peak of $P_{\lambda}(\theta)$, the result of this experiment is not sensitive to the values of sensibly chosen limits to the integral, so that the <u>Bragg reflection integral</u> can be written as

$$\int_{0}^{\pi/2} P_{\lambda}(\theta) d\theta = R_{c}$$
 (2.7)

It is useful, particularly when discussing the measurement of the reflection integral, to express R_c from (2.6), (2.7), as

 $R_{c} = \omega E / I_{0}$ (2.8)

The two important parameters associated with the shape of the profile are the width w_c (more strictly defined as the full width at half maximum .fwhm) and the peak value P_c .

2.1 Measurement of d_{18} , α and $\Delta \theta (\lambda)^{65,39}$

The value of d_{18} and α were determined by the following method. $\vartheta_{\lambda,n}$, defined in Eqn. (2.1), was measured, at several different temperatures at a wavelength for which δ_A (see Eqn. (2.4)) is negligible, and in chosen order. Since δ_A is negligible, each $\theta_{\lambda,n}$ value can be corrected for the value of δ_N to give θ_B and consequently, by the simple Bragg equation (Eqn. (1.5)), d_T . For this purpose either calculated or measured values of δ_N at that wavelength may be used. It will be seen from following that there is good confidence in the use of calculated values, without consequential loss of precision, on fixing d_{18} . A weighted least squares fit on a plot of d against temperature T gives by Eqn. (2.2), d_{18} and α .

Values for $\Delta \theta$ (λ) were obtained in the following manner. At wavelengths where δ_A is non-negligible several measurements of $\theta_{\lambda,n}$ were made at each wavelength. Since it was not possible to maintain the spectrometer temperature constant, the temperature for each $\theta_{\lambda,n}$ measurement was noted. At each point in the wavelength data set θ_B was calculated for the temperature associated with that point using the previously determined d₁₈ and α .

Then for that point $\Delta \theta$ was determined from the expression

$$\Delta \theta = \theta_{\lambda,n} - \theta_{B} \tag{2.9}$$

 $\Delta \theta$ was determined at all points in the data set for the given wavelength and the adopted value of $\Delta \theta$ was simply the mean of these values.

Equation (2.1) describes λ as a function of $\theta_{\lambda,n}$ and therefore any experiment which attempts to determine this function must itself show the dependence of λ upon $\theta_{\lambda,n}$ i.e. it must be dispersive. The incident beam wavelength in such an experiment cannot be measured without knowledge of 2d_T. Therefore λ can only be obtained by use of reference lines with accurately predetermined wavelengths. This leaves $\theta_{\lambda,n}$ as the only unknown and it can then be measured.

It is now important to discuss the criteria for reference line selection and the choice of method for $\theta_{\lambda,n}$ measurement.

a. Selection of reference wavelengths

Reference wavelength lines were selected after careful study of the data sources for Bearden's tables of X-ray wavelengths.⁶⁶ The following points were taken into consideration:

- The error assigned to the value by Bearden and his general comments upon the work. In the wavelength region relevant to this work the error was about 10ppm.
- ii. The instrument employed to measure the wavelength. The most accurate measurements have been carried out on double-crystal spectrometers and tube spectrographs.
- iii. The attention paid to sources of error such as instrument misalignment, temperature variations and dispersion effects.⁶⁷
- iv. The use of reference lines such as $W\;K\!\alpha_1$, and $Cu\;K\!\alpha_1$ as a means of calibration of the work.
- v. The use of an element or compound as a target material. This point is particularly relevant to the wavelength region studied in this work in which a large proportion of the lines were generated from elements unsuitable in their elemental state as target materials for reasons of either low melting points or chemically too reactive. The chemical shifts of Ka_1 , wavelengths in this region are of the order of 100 ppm and so are very significant. In recent years a considerable amount of work has been done on measuring chemical shifts^{68,69} and so, for lines where a compound must be used and the shifts are known accurately, Bearden's tabulated wavelengths (usually given for the element) have been corrected accordingly. The error in the chemical shift determination must be combined with Bearden's listed error.

- vi. The laboratory where the measurement was made. In the relevant wavelength region many of the lines were measured at the John Hopkins University and Uppsala, both highly reputed laboratories with much experience of X-ray wavelength measurements.
- vii. The number of different workers who have studied a line. A useful check of the validity of a wavelength value is the external consistency obtained if a sufficient number of workers have independently made measurements.
- viii. Line breadth. The accuracy with which the peak of a line can be located is inversely dependent upon the line width. The line width increases with wavelength and so where possible shorter wavelengths should be used.
- ix. Line intensity. If the line intensity is high then statistical counting errors will be lower. The most intense lines in the region of interest were the K_{α_1} lines of the elements $11 < Z \leq 35$ and the L_{α_1} lines of the elements $30 < Z \leq 60$.
- x. Accepted wavelength standards[†]. In the wavelength region under consideration the following two lines have been accepted by

where the Å, a new unit of length introduced by Bearden, may differ from the Å unit by ± 5 ppm. The conversion factor between these units is an experimentally determined quantity and will change as further work is done. In this and Bearden's work the wavelength of a line in Å units is related to the energy E of the line by the following relationship.

 $\lambda(\hat{A}) = 12.398105/E(Kev)$

Nevertheless where it is not essential to know wavelength values to 5 ppm accuracy, following common practice the A unit will still be used.

In Bearden's wavelength tables the primary standard is the wavelength of the line W K α_1 which is

 $W K\alpha_1 = 0.2090100 Å$

Bearden as secondary standards

- λ Cu Kä, = 1.540562 Å <u>+</u> 5.2 ppm
- λ Cr K α_1 = 2.293606 Å + 5.2 ppm

A great deal of work has been done on the wavelength determination of Al K_{α_1} and this line is generally accepted as a secondary standard in the longer wavelength region.

 λ A1 K $\alpha_1 = 8.33934 \text{\AA}^{*} \pm 12 \text{ ppm}$

The wavelengths of these secondary standards refer to lines generated from an element target material.

- xi. Suitability of the target material. The target material should in general be easily obtainable, have a high melting point (or high thermal conductivity), and if in the form of a compound the element under consideration should be combined with a light element to ensure a high beam intensity for the required wavelength.
- xii. The complete set of wavelengths chosen must give a clear definition of $\Delta \theta$ (λ) over the required wavelength range.

The lines (in the wavelength region relevant to this study) which meet these criteria are listed in Table 2.1 below.⁺ The wavelengths given are those of lines produced by element target materials. In cases, in this study, where a compound target material was used for line generation, the wavelength value appropriate to line generation from the element, was adjusted to take account of chemical shift.

⁺ Details of the references which report the wavelength determinations are given in the appendix of Ref. 66.

	-	
Line	Wavelength	Error
	(Å)	(ppm)
Cu Ka ₁	1.540562	5
Cr Ka ₂	2.293606	5
Ti Ka 1	2.74851	7
Ca Kal	3.35839	9
Ag La ₁	4.15443	10
Ru La ₁	4.84575	12
Si Kal	7.12542	14
Al Kal	8.33934	12

Table 2. 1Reference wavelength lines

b. Measurement of $\theta_{\lambda,n}$

In principle $\theta_{\lambda,n}$ is obtained by measuring the crystal angles for the Bragg peaks when the crystal is in Positions A (solid lines) and B (dashed lines) as shown in Figure 2.1a. The angular difference between the crystal positions is $180^{\circ} - 2 \theta_{\lambda,n}$. This method eliminates the zero angle error which arises from uncertainty in the precise direction of the incident beam. The crystal angle is read from a circular angle scale which is attached concentrically to the crystal turntable.

The listed wavelength value for a reference line refers to the peak of the line which is only one point on its spectral profile. In order to refer the line profile and peak to the angle scale it is necessary to correlate points on the line profile with crystal angle. Normally the intensity across a line profile changes rapidly with wavelength, so it is important that the variation of wavelength with crystal angle is small. $\theta_{\lambda,n}$ must therefore be



Figure 2.1a Schematic diagram of a 1-reflection spectrometer



Figure 2.1b Vertical projection showing rotational axis misalignment $\boldsymbol{\phi}$



Figure 2.1c Vertical projection showing lattice tilt δ



Figure 2.1d Horizontal projection showing horizontal divergence α of the general ray



Figure 2.1e Vertical projection showing vertical beam misalignment Ψ



Figure 2.1f Vertical projection showing vertical divergence ψ of the general ray

measured in a high dispersion mode. It is also important that the wavelength range reflected by the crystal for a given position is small. $\theta_{\lambda,n}$ must therefore be measured in a high resolution mode. These conditions may be achieved by the following two methods.

- i. The incident beam is collimated so that the beam divergence at the crystal is small therefore allowing only a small angular and wavelength range to fulfil the Bragg condition. This is the basis of the 1-reflection method.
- ii. The incident beam is monochromated so that for any given crystal position only a small wavelength range is received by the crystal. Monochromation may be achieved by employing a first crystal to select a small wavelength range using the Bragg condition. This is the basis of the 2-reflection method.

Details of the dispersion and resolution of the above two methods are given in Ref. 65.

In view of the fact that the major part of the wavelength range being studied was in the soft X-ray region the single crystal reflection method was chosen for the following reasons. Although the resolution afforded by the 1-reflection method is, at short wavelengths, poorer than that d the 2-reflection method, the former method is advantageous at longer wavelengths because its geometrical window (see Expression (2.18)), for given slit settings, does not increase with wavelength, whereas the 2-reflection geometrical window (due to vertical divergence) is roughly proportional to wavelength.⁶⁵ At longer wavelengths absorption becomes significant and so there are considerable beam power losses on successive reflections. It should be noted that at low wavelengths the single crystal method will require high collimation in order to gain sufficient resolution and this will be at the expense of beam power. It is in this wavelength region that the 2-crystal method clearly wins out in terms of resolution and beam power.

The single crystal reflection instrument is shown schematically in Figure 2. Is looking along the turntable axis. An X-ray beam from source X is collimated by slits S_1 and S_2 and is reflected by crystal C through an angle of 2 θ_{λ} .[†] The reflected beam is received by a detector which has a window appreciably larger than the beam size. The Bragg reflection peak is observed by plotting reflected beam intensity against crystal angle as the crystal is slowly rotated about the small angular range where the Bragg condition is satisfied for the given reference line.

The crystal diffracting planes are aligned so that they are parallel to and contain the rotational axis of the crystal turntable. The latter is called the spectrometer axis and is normally aligned parallel to gravity which defines the vertical direction. The slits are aligned so that the line joining their vertical centres and horizontal centres is parallel to the plane of dispersion (orthogonal to the spectrometer axis) and passes through the spectrometer axis. The ray passing through the slit centres is called the central ray. The angular separation of the Bragg peaksfor Positions A and B, that is in fact measured by this instrument, is $180^{\circ} - 2\theta_{\lambda}(\text{meas.})$ and corrections arising from experimental conditions must be applied to θ_{λ} (meas.) in order to obtain θ_{λ} . Since there is a close link between these corrections and measurement uncertainties, they are discussed together in the next section.

⁺ Since primary interest is in the Bragg dispersion function for first order reflection, measurements were made for this order. In further text in this section this order is assumed.
c. Sources of error and their containment

The errors and corrections on θ_{χ} arise from two principal sources; geometrical aberrations and physical sources. Included in the first category are instrumental misalignment, beam geometry, angle scale, peak location and source movement. The errors and corrections of the second category are associated with the physical phenomena, absorption and thermal expansion. Where appropriate procedures are implemented to minimise the sources of error. In most cases, e.g. vertical beam misalignment, it is possible to minimise the source of error to an unknown residual the upper limit on the magnitude of which is governed by the accuracy of the minimising procedure. This residual contributes to the uncertainty on θ_{λ} and thus it is necessary to calculate this contribution. In other cases, where the experiment dictates a source of non-zero value (e.g. vertical divergence) or where minimisation is not possible (e.g. absorption) a correction, calculated from the magnitude of the source, must be applied to θ_{1} (meas.). Note also that the uncertainty on the magnitude of the source in question will contribute to the uncertainty on θ_{λ} .

It is important in any measurement that the errors do not obscure the quantity being measured, hence some tolerance must be placed upon error magnitudes. Typical values of $\Delta \theta(\lambda)$ are about 250 ppm in θ_{λ} and the change in $\Delta \theta_{\lambda}$ over a crystal wavelength range is also about 250 ppm in θ_{λ} and therefore the total error on θ_{λ} must be limited to the order of \pm 20 ppm. In all further discussion of errors the \pm symbols will normally be omitted but all quoted error values must be regarded in this \pm form. It is useful to note that a 20 ppm error on a typical θ_{λ} value, 45 degrees, is 3 arc seconds. Since, $\theta_{\lambda,T}$ is determined by a least squares fit to a set of

 θ_{λ} values which are measured at different temperatures, the error limit on each measurement can be relaxed conditional to a standard deviation on

 θ_{λ} of 20 ppm. Useful values of d_{18} and α may be obtained from θ_{λ} measurements in which the error limit is of the order of 50 ppm. This emphasis upon error tolerances will be reflected in the following discussion of the aforementioned error sources and in later discussions for individual crystals.

i. Diffractor settings

(1) Rotational axis misalignment. The instrument is normally aligned such that the vertical centres of the slits lie in the horizontal plane. If the rotational axis is not vertical then the angle between the crystal plane of dispersion and the horizontal plane will be different for Positions A and B. This will introduce vertical misalignment Ψ and a crystal lattice tilts. Ψ, δ are defined below along with $\sigma \theta_{\lambda}(\Psi)$, $\sigma \theta_{\lambda}$ (δ) the respective errors arising in θ_{λ} from the residual Ψ and δ after machine alignment.

Figure 21b shows a crystal with a rotational axis which makes an angle ϕ with gravity (z). X X' is the horizontal plane. In the figure the crystal rotational angle θ is such that δ ', the angle between the crystal normal and X X' is a maximum. These values of θ and δ ' shall be called

 θ_{o} and δ'_{o} respectively. If ϕ and δ'_{o} are small the general expression for δ' is

$$\delta' \simeq \phi \cos (\theta - \theta_0) + \delta'_0 - \phi. \qquad (2.10)$$

The value of θ_0 with respect to the spectrometer angle scale is dependent upon the line of the axis projected into the plane of dispersion. In

general this is not known and so it is not possible to assign an absolute value to δ' . However the amplitude of the cosine function is ϕ and therefore the maximum effective crystal tilt change is 2ϕ . Clearly the maximum possible change in vertical misalignment is also 2ϕ . On the basis that the slit system lies in the horizontal plane, ϕ is minimised by aligning the rotational axis of the turntable to the local gravity vector. Full details are given in Subsection 3.3.3. The unknown residual $\sigma\phi$ that remains after alignment is treated as a contribution to the uncertainty on θ_{λ} and must be limited such that this uncertainty is within the following tolerance. With $\sigma\phi < 30''$ the resultant $\sigma\theta_{\lambda}(\delta)$ and $\sigma\theta_{\lambda}(\Psi)$ on a 45^o Bragg angle are negligible i.e. < 1 ppm and typically for $\sigma\delta < 3'$ and

 $\sigma \Psi < 1!$ then the resultant $\sigma \theta_{\gamma}(\delta, \Psi)$ (see below) is also negligible.

(2) Mounting eccentricity. If the crystal diffracting planes are displaced horizontally from the spectrometer axis by E then the lateral displacement D of the reflected beam is given by $D = 2 E \cos \theta$. The glancing angle is not affected by the crystal eccentricity, and as the detector window is wide enough to cope with the beam displacement no correction to the measured angle is necessary. Nevertheless it is important that the eccentricity is as small as possible otherwise the incident beam will strike different areas of the crystal surface for Positions A and B. Mounting eccentricity is minimised by using optical alignment techniques to align the crystal mount reference plane, against which the crystal face locates, such that it is parallel to and contains the rotational axis (see Subsection 3.3.3). The maximum distance along the crystal surface between the areas of crystal irradiated at reflection positions A and B for a residual σE is $2 \sigma E/\tan \theta$. For a typical beam width of 0.2 mm, if $\sigma E < 20 \mu m$

then the reflecting crystal surface area at Positions A and B will not change

by more than 20% for $\theta > 5^{\circ}$. The total shift of the beam across the detector window between Positions A and B for an eccentricity E is 4 E $\cos \theta$. Again it is important that the eccentricity is minimised because at soft X-ray energies non-uniformity in the window transmission may introduce errors which are difficult to estimate.

(3) Lattice tilt. This will be defined in its positive sense using the convention of Ref. 65. The lattice tilt δ is the angle by which the normal to the diffracting planes lies above the plane of dispersion. Lattice tilt gives rise to a shift in the peak position which may be calculated from (2.11) below. The minimisation of δ involves setting the crystal lattice planes parallel to the rotational axis. Since lattice planes are not necessarily parallel to the crystal face, the alignment incurs optical and X-ray alignment methods as given in Subsection 3.3.3. The uncertainty on θ_{λ} arising from the residual $\delta\delta$ is given by

$$\sigma\theta_{\gamma}(\delta) = (\sigma\delta^2 \tan\theta_{\gamma})/2 \qquad (2.11)$$

A typical uncertainty in the lattice tilt $\sigma\delta$ of 3' would result in an error of 0.5 ppm for a 45° Bragg angle.

The relation (2.11) may also be used to calculate the required correction to θ_{λ} (meas.) for a known δ . The R.H.S. of (2.11) must be subtracted from θ_{λ} (meas.).

(4) Scan speed irregularities. Since the crystal is scanned automatically through the peak it is important that the scan speed is uniform and that there is no irregular movement during the scan. It is difficult to estimate the resultant uncertainties and so it is essential to minimise the above phenomena such that the uncertainties are negligible i. e. of the order of 0.1" over a complete scan. During a scan the detector and crystal rotate at a 2:1 scan speed ratio. Non-uniformities in the transmission across the detector window will cause distortion of the peak profile if this ratio is not maintained constant. Again uncertainties are difficult to estimate but a tolerance on the drift of the detector of 10 arc sec (0.00025 in) gives rise to negligible uncertainty.

ii. Beam settings

(1) Horizontal beam misalignment. This is the angle X, in the plane of dispersion through which the slit system as a unit must be rotated, about an axis parallel to the spectrometer axis, in order to make the central ray pass through the spectrometer axis. For X = O let the line joining the horizontal slit centres and the spectrometer axis be called the line of co-linearity. X is minimised by adjusting the positions of the slits such as to locate a beam of light, that passes through slits of small width, symmetric about a fine wire which assumes the line of the rotational axis (see Subsection 3.3.4). The measured angle 180 - $2\theta_{\lambda}$ (meas.) will not be affected by the magnitude of the residual σX because the shift in the crystal angle necessary to attain the Bragg condition in Position A will be compensated by an identical opposite shift for Position B. The incident beam will strike the same area of the crystal for Positions A and B but will be shifted along the crystal face from the spectrometer axis by R sin $\sigma \chi/\sin \theta$ where R is the distance between the spectrometer axis and the point at which the central ray crosses the line of co-linearity. For purposes of estimation this point can be taken as the midpoint of the slit separation. If the detector is aligned, as is normally the case, centrally about the angle 2θ where θ is the angle between the crystal and the line of co-linearity then for Positions A and B the beam will strike the same area of the detector which is a distance DD' from the centre of the detector given by

 $DD' = R \sin \sigma \chi \cos \sigma \chi + (H + R \sin^2 \sigma \chi) \tan \sigma \chi$ (2.12) where H is the distance between the spectrometer axis and the detector. Note that DD' is independent of the Bragg angle. The error resulting from horizontal movement of the X-ray target focal spot is difficult to estimate but, with the experimental conditions used, it will be small. This is because the slit widths, which are of the order of 0.2 mm, are small in comparison to the width of the focal spot which, measured from photographs of the source, is approximately 2.0 mm. Thus movement of the focal spot will cause little change in the intensity distribution across the slit. In view of the size and sporadic nature of this error, it has been neglected in the final error analysis but, is still regarded as a factor which may contribute to the spread of repeated results.

(2) Horizontal Divergence. The horizontal divergence of a ray is the angle α in the plane of dispersion between that ray and the central ray. α_m , the maximum value of α is controlled by the slit widths. Horizontal divergence broadens the peak but provided the source is uniform over the slit width then the profile will be symmetric, thus there will be no change in the determined peak position. There will however be a greater error in determining the peak position due to peak broadening. Clearly for reasons of beam power requirements α must be non-zero but its magnitude must be limited in order to keep peak broadening to a minimum. It is shown from photographs of the source intensity distribution that the focal spot, which is of uniform intensity, is approximately 2mm wide. Since typical slit settings are of an order of magnitude less, it is reasonable to assume that the intensity distribution over the slit width is uniform and thus gives rise to negligible error in the peak location. The uncertainty in θ_{λ} arising from peak broadening is difficult to estimate but peak broadening as mentioned above contributes to the uncertainty in the peak location, an estimate of which is given in the discussion on peak location.

(3) Vertical beam misalignment. The vertical beam misalignment Ψ is the

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angle by which the central ray lies below the plane of dispersion. It causes a shift (calculated from (2.13)) in the peak position to a larger angle and is minimised by aligning the vertical slit centres to a plane perpendicular to the spectrometer axis (see Subsection 3.3.4). The uncertainty on θ_{λ} arising from the residual $\sigma\Psi$ is calculated from the following expression

$$\sigma \theta_{\lambda}(\Psi) = (\sigma \Psi^2 \tan \theta_{\lambda})/2$$
(2.13)

In the 1-reflection instrument used, the slit separation was 700 mm and each slit was aligned to ± 0.1 mm. Using these figures and a Bragg angle of 45° then $\sigma \theta_{\lambda}(\Psi)$ is 8×10^{-3} " which clearly can be neglected.

(4) Vertical divergence. The vertical divergence of a ray is the angle ψ by which the ray lies below the plane of dispersion. The maximum vertical divergence ψ_m allowed by the slit system is given by

$$\psi_{\rm m} = [(a + b)/2]/L$$
(2.14)

where a and b are the heights of Slits S_1 and S_2 respectively and L is the slit separation. Vertical divergence causes an increase in the angle of the peak position and since for reasons of beam power requirements slit settings and hence ψ must be non-zero, the following correction must be applied to θ_{λ} (meas.)

$$\Delta \theta_{\lambda}(\psi) = ((a^{2} + b^{2}) \tan \theta_{\lambda}) / (24L^{2})$$
(2.15)

For typical slit settings a - b = 5 mm and L = 700 mm, θ_{λ} =45° then

 $\Delta \theta_{\lambda}(\psi) = 0.9$ ". The uncertainty in the slit settings <u>+</u> 0.1 mm gives rise to a negligible uncertainty on θ_{λ} .

(5) Combined lattice tilt and vertical misalignment uncertainty. If δ and Ψ are both non-zero, there is a shift (calculated from (2.16)) in the peak position (towards a smaller angle if the product $\delta \Psi$ is positive). δ and Ψ are minimised as outlined above. The uncertainty on θ_{λ} arising from the combination of the residuals $\sigma\delta$ and $\sigma\Psi$ is given by

$$\sigma\theta_{1}(\delta,\Psi) = \sigma\delta\sigma\Psi/\cos\theta_{1} \qquad (2.16)$$

Using the figures already quoted for $\sigma\delta, \sigma\Psi$ and θ_{λ} the resulting uncertainty $\sigma\theta_{\lambda}(\delta,\Psi)$ is 0.075" which again may be neglected.

(6) Resolution. The precision with which θ is defined for the peak position of the Bragg diffraction profile is plainly degraded by any factor such as horizontal divergence which broadens the peak. To minimise peak broadening the measurements of θ_{λ} should be conducted at the highest wavelength resolution obtainable. The resolution of a spectrometer is its ability to separate two lines which are close in wavelength, the wavelength difference being $\Delta \lambda$. Quantitatively it may be indicated by 70

$$\Delta\lambda/\lambda = w_n/\tan\theta_\lambda \tag{2.17}$$

In Equation (2.17) w_n is the width of the instrumental window function where the width for this and other functions denotes the full width at half-maximum intensity (fwhm). In the case of the single crystal reflection instrument the instrumental window function is the convolute of the geometrical window function and the crystal line spread function. If the width 'b' of Slit S₂ is equal to or greater than that of S₁ then the width of the geometrical window function is given by

$$w_{g} = \frac{b}{L}$$
(2.18)

where L is the separation of the slits controlling horizontal divergence.

In the interest of beam power it pays to increase w_g until it approaches w_c , the width of the crystal line spread function, but not to the extent that w_g contributes dominant peak broadening. Unfortunately in order to obtain reasonable beam power w_g was set to about 40" which is approximately twice typical w_c values. This contributes considerably to the uncertainty in the peak location which is discussed later. Nevertheless this setting for w_g gave good separation of α_1 , α_2 doublets for the short to mid-range wavelengths; for

longer wavelengths doublet separation was poorer but in any case resolution at these wavelengths was limited by w_c .

<u>iii. Angle reading</u>. Discrepancies arise between the true and measured angle through which the crystal is rotated to obtain reflections at Positions A and B, due to the following factors:

- a. eccentricity of the circular angle scale about the turntable rotational axis
- b. non-circularity of the angle scale
- c. errors in the positions of the angle scale lines
- d. maladjustment of the optical micrometer verniers
- e. micrometer reading error
- f. errors arising from scaling the chart recorder baseline

The first three factors are taken into account by calibrating the angle scale and a commonly employed method⁷¹ uses pairs of microscopes to read the scale at various intervals thus intrinsically calibrating the scale. The method employed in this laboratory differs fundamentally in that the angle generated by rotation of the turntable from one angle setting to another is measured independently by attaching a calibrated angle gauge block to the turntable and noting an autocollimator's reading obtained by reflection off the sides of the gauge block for the two angle scale settings. In this way the angle scale correction $\Delta \theta_{\lambda}$ (ang.), which must be made to θ_{λ} (meas.) is obtained. Full details of the method are given in Subsection 3.3.2. The following factors give rise to uncertainties in the angle scale calibration.

(1) <u>Angle gauge block calibration</u>. The accurately known angle of the block has a value near to that of $2\theta_{\lambda}$ (meas.). The block is made up of one or more angle gauges and the uncertainty on the block is obtained by combining the calibration uncertainties of the individual gauges. The

calibration uncertainty cited by the National Physical Laboratory is ± 1 " for each guage. A typical block consists of 4 angle guages. It should be noted that the true angle of each guage as measured by the National Physical Laboratory differs by the order of 1" from the nominal angle and this discrepancy must therefore be taken into account in the angle scale calibration.

- (2) <u>Angle setting</u>. The uncertainty at each crystal angle setting due to the micrometer reading error is 1" and so the uncertainty on $2\theta_{\lambda}$ (meas.) is $\sqrt{2}$ ".
- (3) <u>Autocollimator reading</u>. The uncertainty associated with each autocollimator reading is 1" and again the uncertainty on $2\theta_{\lambda}$ (meas.) is $\sqrt{2}$ ".

Factor d. arises from the uncertainty in setting the 10' division and the 2" division verniers of the optical micrometer (see Subsection 3.3.2). The uncertainty in setting the 10' division vernier is 1". Setting the 2" division vernier requires two micrometer readings and since the uncertainty on each reading is 1" the uncertainty in setting the vernier is $\sqrt{2}$. The measurement of 2 θ_{λ} (meas.) requires two readings of the micrometer and so the uncertainty due to vernier maladjustment on each micrometer reading must be combined giving an uncertainty of $\sqrt{6}$ ". It should be noted that uncertainties due to factor d. would be avoided if the angle block was made up to exactly 2 θ_{λ} (meas.) but for reasons given in Subsection 3.3.2 this would generate other uncertain ties. Factor e. contributes an uncertainty $\sqrt{2}$ " on 2 θ_{λ} (meas.). Factor f. arises from errors in the angle division marks of the chart recorder baseline. These marks were made at regular angular intervals during the course of each scan by reading from the turntable angle scale. The

[†] Uncertainties were combined by the method of probable errors defined in Subsection d. below.

peak angle was determined by interpolation between baseline angle scale marks. The uncertainty on each chart recorder mark is 1" and the resultant uncertainty on 2 θ_{λ}^{+} (meas.) is 2". All the above uncertainties were combined and halved to give a total angle reading uncertainty on θ_{λ} (meas.) of ~ 2", an uncertainty on $\theta = 45^{\circ}$ of 13 ppm.

iv. Peak location. In order to correlate wavelength with crystal angle it is necessary to refer the incident beam reference wavelength to a point on the single crystal rocking curve. This curve is asymmetricas a result of two factors:

a. spectral line asymmetry

b. crystal window function asymmetry due to absorption

Through historical tradition⁶⁶ the wavelength of a line is listed as the peak of the spectral line profile and although this profile is modified to some extent by convolution with the instrumental function it was nevertheless decided that the peak of the observed single crystal rocking curve should be adopted as corresponding to the reference wavelength. To locate the peak, chords parallel to the abscissa were drawn across the curve at various heights and a curve was drawn through the midpoints of these chords. The peak was defined by the point at which the bisector curve intersects the rocking curve (see Fig.2.2). This peak is often called the 'extrapolated peak' and a statistical error analysis of this peak location method has been done by Yap ^{72,73}. The chief advantage of this method is that the main body of the curve is employed thus eliminating the need to rely purely on the data points at the top of the curve where statistical errors severely affect judgement of the peak intensity.

The error in the peak location is dependent upon counting statistics in that the standard deviation of each data point is \sqrt{RT} where R is the count rate at that point on the curve and T is the time sample. Data point errors



Figure 2.2 Location of the 'extrapolated peak' by means of a smooth bisector curve through the chord midpoints



Figure 2.3 Temperature sensitivities of various Bragg analysers (Jenkins, R. and de Vries, J.L. : Practical X-ray Spectrometry, 1970)

will in turn give rise to errors in the mid-points of the chords drawn across the curve.

The time required to plot the peak will also give rise to errors in that a long scan duration will render the scan susceptible to changes in source intensity and other variations e.g. temperature. In order to minimise the peak location error, factors which contribute to peak broadening (e.g. poor resolution) must be minimised and a compromise must be reached between good counting statistics and a reasonable scan duration. The peak location error was estimated from the spread of the chord mid-points about the line drawn through them. A typical uncertainty in peak location was ~ 2" an error of 12 ppm on a 45° Bragg angle.

v. Absorption. Structures in the beam path give rise to absorption and since the latter is a rapidly varying function of wavelength the absorption difference across a line profile gives rise to asymmetry and consequently a small peak shift. Shacklett 74 , on the basis of the approximately cubic dependence of absorption with wavelength estimated the peak shift to be $\Delta \theta \approx 0.6 \mu_{g} x (a/\lambda)^2 tan\theta$ is in arc seconds, μ_{σ} is the linear absorption coefficient where Δθ of an absorber of length x in the beam path, λ is the line wavelength in angstroms and 'a' is the half width at half maximum in milli-angstroms. The main contributions to absorption (excluding that of the crystal which is dealt with below) arise from the 6μ : Melinex source window and self-absorption at the source target but these cause negligible peak shifts. It should be noted that self-absorption in the target may also arise, in addition to normal absorption, from overlap of the emission line with absorption lines or absorption edges of target material elements. In the present study all emission lines were far removed from spectral absorption features of target

elements.

The Prins theory of crystal diffraction predicts that if absorption is non-negligible then the long wavelength side of the single crystal diffraction pattern will be lower than the short wavelength side. This results in asymmetry and a slight shift of the peak of the spectral line towards a smaller Bragg angle. Due to the complex nature of the Prins formula it is difficult to obtain an analytical expression for the shift. In this work the shift was obtained by calculating the Prins diffraction profile as a function of angle for the required wavelength and graphically measuring the angular difference between the centroid and the centroid reference which is the Bragg angle corrected for the index of refraction.⁷⁵ The measured angle is corrected by addition of this shift $\Delta \theta_{\lambda}(abs.)$.

vi. Temperature variations. Temperature changes during the course of a θ_{λ} determination cause a change in θ_{λ} due to thermal expansion of the analyser.

Temperature variations are minimised by allowing sufficient time for thermal stabilisation of the instrument and its environment, and by limiting scan durations so that the temperature difference between reflection Positions A and B is small. Half this temperature difference combined with the temperature reading uncertainty (0.1°C) was regarded as the temperature uncertainty σT for a θ_{λ} measurement. The resultant error $\sigma \theta(T)$ in

 θ_λ is calculated by differentiation of the Bragg equation with respect to temperature, giving:

$$\sigma \theta_{\chi}(T) = -\alpha \tan \theta_{\chi} \sigma T \qquad (2.19)$$

Equation (2.19) states that $\sigma \theta_{\lambda}$ (T) is proportional to α and it is this parameter which will determine the tolerated temperature uncertainty. In the case of PET where α is nearly an order of magnitude greater than that of other X-ray analyser crystals, serious problems were encountered. This is clearly illustrated by Jenkins and de Vries⁹ in a plot of the variation of $2\theta \text{ per}^{O}C$ with 2θ for various crystals (Fig. 2.3). From their graph it was calculated that a temperature uncertainty of 0.5^OC would give rise to an error of approximately 80 ppm on θ_{λ} for PET at 45^O.

The treatment of uncertainties arising from temperature variations is dealt with in the following section.

d. Final measurement uncertainties on d_{18} , α and $\Delta \theta(\lambda)^{76,77}$ i. Correction and measurement uncertainty on θ_{λ} The final correction to θ_{λ} (meas.) can be summarised in the following expression:

 $\theta_{\lambda} = \theta_{\lambda} (\text{meas.}) - \Delta \theta_{\lambda} (\psi) + \Delta \theta_{\lambda} (\text{abs.}) \pm \Delta \theta_{\lambda} (\text{ang.})$ (2.20) in which all terms are defined above.

The measurement uncertainties on θ_{λ} discussed above are combined by the method of probable errors to give the final measurement uncertainty $\sigma \theta_{\lambda}$. The method of probable errors may be summarised as follows. If σA , σB and σC are independent errors incurred in the measurement of X then the probable error on X is given by

$$\sigma X/X = [(\sigma A/A)^2 + (\sigma B/B)^2 + (\sigma C/C)^2]^{\frac{1}{2}}$$
 (2.21)

Since differing experimental conditions and settings cause differences in final measurement uncertainties then, rather than give a typical uncertainty value, details of the particular values are given with the experimental results. <u>ii. Measurement uncertainties on d_{18} and α </u> Both d_{18} and α were determined from a plot of d against temperature T as outlined in the introduction to Section 2.1. The uncertainty on the d values arise from the uncertainties on $\theta_{\rm B}$, λ and T. Since the uncertainty on $\delta_{\rm N}$ is small with respect to $\sigma \theta_{\lambda}$ then the approximation $\sigma \theta_{\rm B} = \sigma \theta_{\lambda}$ was made. It should be noted that for the present case $\sigma \theta_{\lambda}$ excludes the contribution from temperature variations since the latter is taken account of in the least squares analysis. The uncertainty $\sigma d(\theta_B)$ contributed to d by $\sigma \theta_B$ can be calculated from the first θ differential of the Bragg equation thus

$$\sigma d(\theta_{B}) = (n\lambda \cos\theta_{B}/2\sin^{2}\theta_{B})\sigma\theta_{B} \qquad (2.22)$$

where $\sigma \theta$ is in radians. The uncertainty $\sigma d(\lambda)$ on d due to the uncertainty $\sigma \lambda$ on λ is calculated from the first λ differential of the Bragg equation thus

$$\sigma d(\lambda) = (n/2\sin\theta_B)\sigma\lambda \qquad (2.23)$$

where $\sigma\lambda$ in Angstrom units is the uncertainty on the reference wavelength which if appropriate includes the chemical shift uncertainty. The contribution to σd arising from T is dealt with below in the least squares analysis. The total uncertainty σd on d is calculated by combining the uncertainties contributed by θ_{B} and λ using the method of probable errors. The method outlined for calculating σd may be summarised in terms of partial derivatives. If f is a function of m_1, m_2, \ldots, m_n , and $\sigma_1, \sigma_2, \ldots, \sigma_n$ are the uncertainties on these terms then σ the total uncertainty on f (m_1, m_2, \ldots, m_n) is given by

$$\sigma^{2} = \left(\frac{\partial \mathbf{f}}{\partial m_{1}}\right)^{2} \sigma_{1}^{2} + \left(\frac{\partial \mathbf{f}}{\partial m_{2}}\right)^{2} \sigma_{2}^{2} + \dots + \left(\frac{\partial \mathbf{f}}{\partial m_{n}}\right)^{2} \sigma_{n}^{2} \qquad (2.24)$$

A number of factors determine the form of the least squares analysis of the plot of d against T and consequently these factors also affect the uncertainty estimation for d_{18} and α . The uncertainties on T were considerably larger than the uncertainties on d and therefore a linear regression of T upon d is appropriate. The uncertainties on the points of the plot are unequal due to variations in the temperature uncertainties and therefore to take account of this a weighted linear regression is required. The uncertainties on the d values were combined into the T uncertainties (see Paragraph c. vi above) by means of the first temperature differential of Eqn. (2. 2) using the value of

 α derived from an unweighted linear regression of T upon d. The factor $1/(\sigma T)^2$ was used to weight each point in the weighted linear regression and from this regression the values and standard errors of d₁₈ and α were obtained.

<u>iii. Measurement uncertainty on $\Delta \theta(\lambda)$ </u> Equation (2.9) shows that the total uncertainty $\sigma \Delta \theta$ on each $\Delta \theta$ value at a given wavelength (see introduction to Section 2.1) arises from the uncertainties $\sigma \theta_{\lambda}$ and $\sigma \theta_{B}$. For the following data reduction $\sigma \theta_{\lambda}$ includes the contribution arising from temperature variations. The uncertainty $\sigma \theta_{B}$ arises from σd and $\sigma \lambda . \sigma d$ is determined from the plot of d against T (see Paragraph ii above) using the expression

$$\sigma d_{T} = (\sigma \overline{d} + ((T - \overline{T})\sigma (\alpha d)^{2})^{\frac{1}{2}}$$
(2.25)

where T is the temperature at which θ_{λ} is measured. T, the value of T, at the centroid of the data points, is given by $\sum W_i T_i / \sum W_i$ where W_i is the weighting factor for each data point. \overline{d} is the value of d at T = T and $\sigma \overline{d}$ is the uncertainty on \overline{d} . $\sigma(\alpha d)$ is the uncertainty on the slope of the plot. $\sigma \theta_B(d)$ the uncertainty on θ_B arising from σd is calculated using the reverse form of Expression (2.22). $\theta_B(\lambda)$, the uncertainty on θ_B arising from $\sigma \lambda$, is calculated from the first λ differential of the Bragg equation thus

$$\sigma \theta_{\mathbf{p}}(\lambda) = \sigma \lambda / (2 \mathrm{d} \cos \theta)$$
 (2.26)

Combination of $\sigma\theta_{B}(d)$ and $\sigma\theta_{B}(\lambda)$ gives $\sigma\theta_{B}$ which combined with $\sigma\theta_{\lambda}$ gives $\sigma\Delta\theta$ for a given $\Delta\theta$ value. Since the uncertainties on the $\Delta\theta$ values of a given wavelength are unequal the best value of $\Delta\theta$ is the weighted mean of these values and this is given by $\sum W_{i}\Delta\theta_{i}/\sum W_{i}$ where $W_{i}(=1/(\sigma\Delta\theta)^{2})$ is the weighting factor for the ith value of $\Delta\theta$. The uncertainty on the weighted mean, $\sigma\Delta\theta$, is $1/(\sum W_{i})^{\frac{1}{2}}$.

2.2 The Line Spread Function

2.2.1 Measurement of its integral

The integral of the line spread function was defined in Expressions (2.7) and (2.8) on the basis of an idealised experiment using a beam, the beamspread and bandwidth of which are both infinitesimal. In practice the beam is characterised by finite beamspread and bandwidth. The intensity of such a a beam, incident upon a crystal, is given by

$$I_{o} = \int_{\lambda_{1}}^{\lambda_{2}} \int_{0}^{\psi_{m}} \int_{0}^{\alpha_{m}} G(\alpha, \psi) J(\lambda) d\alpha d\psi d\lambda$$
(2.27)

where α and ψ the horizontal and vertical divergences of a given ray are defined in Section 2.1. α_{m} and ψ_{m} , the maximum values of these quantities, are determined by the collimator geometry. $G(\alpha, \psi)$ is the angular distribution function which depends upon the source angular intensity distribution and the collimator transfer function. $J(\lambda)$ is the source spectral function. The reflected intensity for such a beam is

$$I(\theta) = \int_{\lambda_1}^{\lambda_2} \int_{0}^{\psi_m} \int_{-\alpha_m}^{\alpha_m} P(\theta) G(\alpha, \psi) J(\lambda) d\alpha d\psi d\lambda$$
 (2.28)

where θ is the glancing angle of the general ray onto the crystal. By analogy with the derivation of (2.8) the following expression is derived from

$$R_{c}^{\prime} = \frac{\int_{\theta_{1}}^{\theta_{2}} \int_{\lambda_{1}}^{\lambda_{2}} \int_{0}^{\psi_{m}} \int_{-\alpha_{m}}^{\alpha_{m}} P(\theta) G(\alpha, \psi) J(\lambda) d\alpha d\psi d\lambda d\theta}{\int_{\lambda_{1}}^{\lambda_{2}} \int_{0}^{\psi_{m}} \int_{-\alpha_{m}}^{\alpha_{m}} G(\alpha, \psi) J(\lambda) d\alpha d\psi d\lambda}$$
(2.29)

R'_cmay be defined as^mthe measured reflection integral for the general beam condition experiment.

A knowledge of the variation of R'_c with differing beam conditions is necessary for the determination of R_c . It is found in general that provided the wavelength region being studied is not too near to an absorption edge of a crystal atom then $\int_{\theta_1}^{\theta_2} P(\theta) d\theta$ varies slowly with wavelength and so for the case of a parallel beam the numerator of (2.29) may be written as

$$\int_{\theta_1}^{\theta_2} P_{\lambda}(\theta) d\theta \int_{\lambda_1}^{\lambda_2} J(\lambda) d\lambda$$
(2.30)

Substitution of (2.30) into (2.29) yields $R'_{c} = R_{c}$ a result which is valid if $P_{\lambda}(\theta)$ is constant between the wavelength limits λ and λ . 1 2 In their consideration of the dependence of R'_{c} upon beamspread Compton and Allison (Ref. 52, p.398) noted that in keeping with the properties of convolution integrals, if the widths of the functions $P_{\lambda}(\theta)$ and $G(\alpha, \psi)$ differ greatly then the integrals can be separated and thus $R'_{c} = R_{c}$. Evans and Leigh⁷⁹ extended these considerations by investigating theoretically and experimentally the case in which the widths of $P_{\lambda}(\theta)$ and $G(\alpha, \psi)$ are similar. They established that $R'_{c} = R_{c}$ and is invariant with beamspread for this condition also.

It can thus be concluded that within the given limits, R_c does not change with varying beamspread and bandwidth of the incident beam. In the following section which deals with 1-reflection measurement of R_c , the experimental methods described are based upon these conclusions.

a. 1-reflection methods

In the laboratory R_c values can be measured in a 1-reflection mode by scanning the crystal through the Bragg reflection angle range of a given emission line in the incident beam spectrum. This spectrum normally includes other emission lines and a Bremsstrahlung continuum all of which must be regarded as contamination in that all components of the spectrum contribute to I_o but only the spectral range encompassed in the crystal scan contributes to E. Clearly an uncorrected I_o value would give rise to a measured R_c value severely in error. The following methods were devised in an attempt to overcome this problem.

i. Use of fluorescent excitation. If the X-ray beam is generated by fluorescent excitation then the continuum contribution is negligible, but the spectrum still contains other emission lines. In the hard X-ray region it is possible, in certain cases, by choice of a suitable filter, to isolate a desired emission line. This method, which has been employed successfully by Kestenbaum for emission lines in the 1.66 to 5.71 Å wavelength region, is inapplicable at longer wavelengths because isolation of an emission line cannot be achieved but overriding this is the fact that fluorescent excitation sources are very inefficient in this wavelength region. ii. Direct methods using electron excitation. A beam of high intensity but with a significant continuum contribution may be obtained by direct electron excitation. It may be argued that if such a beam is approximately mono-chromated using suitable filters then R_c can be measured by scanning the crystal at a constant rate through the filter pass band spectral region and provided R_c is constant over this range then Eqn. (2.8) can be applied. This wide-scan method has the following disadvantages:

- It is inefficient in that filter pass bands are broad and therefore excessively long scan durations are required.
- (2) It is inapplicable if the long wavelength cut-off of the filter pass band exceeds the crystal 2d value.

Reference 79 outlines a method which in principle is equivalent to the wide scan method but eliminates the above disadvantages. The spectrum of a filter pass band is mapped by setting the crystal to reflect a particular wavelength of the pass band and the reflected beam is counted over a suitable time interval. This procedure is repeated for other wavelengths of the pass band until the relative strengths of all components in the reflected beam are measured. The same relative strengths will apply to the incident beam and thus the I_o value for the desired emission line can be calculated. If the filter pass band exceeds the test crystal 2d value then a preliminary calibration of the pass band spectrum can be made using a crystal with sufficiently large 2d. This method, which seriously takes account of continuum radiation, facilitates the direct measurement of R_c using a single crystal. The procedure entailed is still relatively time consuming but the R_c values obtained can be regarded as standards by which to judge the values obtained from indirect, rapid methods.

iii. The relative method. In this method R_c is measured by using a beam

for which the incident intensity of the spectral component reflected is known. The direct absolute method outlined above may be employed to measure the R_c of a prospective standard crystal and this crystal in turn used to calibrate the incident beam of the test crystal. In the calibration, Eqn. (2.8) is applicable to the determination of I_0 for the small spectral region of interest regardless of beam contamination. The test crystal is then inserted and its R_c is measured. To correct for the variation in beam intensity and composition during the course of the whole operation it is necessary to re-calibrate the beam using the standard crystal.⁸¹

This method, although more efficient than the absolute method, suffers in that errors are accumulated over the three experiments and indeed may be impossible to apply if the source is affected by the repeated release and generation of the tank vacuum.

b. 2-reflection methods

1-reflection methods are in general too inefficient for routine R_c measurements, for by necessity they are designed to take account of the contamination radiation in the incident beam. If the beam can be monochromated sufficiently, to remove this contamination then, it is possible to decrease the time required for a measurement. It is upon this principle that the use of two crystal methods is based. In such a method a stationary monochromator crystal (Crystal A) is used to select, by means of the Bragg condition, a small wavelength range from the source beam. The reflected beam then forms the incident beam for the test crystal (Crystal B) which is scanned through the Bragg reflection region as in the single crystal mode.

Bragg reflection at Crystal B can be achieved in either of the crystal configurations shown in Fig. 2.4. In Configuration 1 the beams incident on Crystal A and reflected from Crystal B are on the same side of the beam



(a) Configuration 1 The plus position



(b) Configuration 2 The minus position

Figure 2.4 Principal configurations of the 2-reflection spectrometer. The line RR' is parallel to the face of Crystal A

between the two crystals. In Configuration 2 they are on opposite sides.

If the face of Crystal A is adopted as a reference line then for Configuration 1 the angle w through which Crystal B has rotated to achieve this configuration is

$$\mathbf{w}_1 = \mathbf{\theta}_m + \mathbf{\theta}_n \tag{2.31}$$

Similarly for Configuration 2

$$\mathbf{w}_2 = \pi - (\theta_n - \theta_m) = \pi + \theta_m - \theta_n$$
(2.32)

The dispersion D of the instrument, calculated by differentiation of the simple Bragg equation for the two cases is thus

$$D = \frac{dw}{d\lambda} = \frac{\tan\theta_m + \tan\theta_n}{\lambda}$$
(2.33)

where the upper and lower signs refer to Configurations 1 and 2 respectively. Clearly the dispersion of the instrument is greater for Configuration 1 hence its application to spectroscopic studies. Reflection integrals are normally measured in Configuration 2 as the angular range of the Crystal B scan necessary to embrace the spectrum of the beam incident upon it is less than that for Configuration 1.

Allison and Williams⁸² devised a notation referring to Configurations 1 and 2 as the plus and minus positions, in keeping with the nature of Eqn. (2.33). More specifically a configuration labelled (m, -n) means that Crystal A is set for a reflection of order m and Crystal B is set in the minus position for a reflection of order n.

As a consequence of using a crystal monochromator, the beam incident upon Crystal B is polarised. This is due to Crystal A response varying with the polarisation angle of the unpolarised beam from the source. Equation (2.8) only applies to individual polar components of the polarised beam. Conceptually it is possible to distinguish between these components but in practice only the total intensity of the incident and reflected beams can be measured. In accordance with this limitation the 2-reflection integral may be given by

$$\mathbf{E}_{\omega}/\mathbf{I}_{o} = \sum_{\mathbf{p}} \mathbf{E}^{\mathbf{p}}_{\mathbf{p}} \omega/\sum_{\mathbf{p}} \mathbf{I}^{\mathbf{p}}$$
(2.34)

where I_0 is the intensity of the beam incident upon Crystal B and superscript p refers to the polar components. A 2-reflection integral can be measured very quickly and in view of this it is worth investigating the relationship between this quantity and R_o, in order to calculate the latter. From the above discussion it is clear that such a relationship will be dependent upon the beam polarisation and it will therefore act as a pointer towards measurement methods for which beam polarisation can be eliminated or corrected for. The problem of relating R_c to a 2-reflection integral is normally approached by way of a geometrical description of the 2-crystal spectrometer. The equation of the instrument window is applied to the special case of two identical crystals in the (n, -n) parallel position.^{21,52}Since this study is concerned chiefly with first order reflection integrals the (1, -1) position will be discussed. The unique properties of this position allow the equation to be simplified so facilitating the derivation of the R_c , R_{cc} relationship where R_{cc} is the 2-reflection integral for this position (see below). The geometrical description of the instrument is sufficiently tedious to obscure the simple relationship between the 2-reflection rocking curve and the line spread function and so details are given in Appendix B. A brief study of the geometrical approach included in the discussion of the (1, -1)parallel mode will enable comparison of it with a more direct and simpler approach⁸³ which is outlined in dealing with the more general (1, -1) asymmetric and orthogonal configurations.

i. The (1, -1) parallel mode. Consider the 2-reflection system where the two crystals are identical, the crystal faces are parallel to their respective turn-table rotational axis and the crystals are operated in the parallel mode (see

above). Taking the case of an unpolarised beam incident on Crystal A this beam may be regarded as being composed of two orthogonally plane polarised components, the σ - and π - components. The electric vector of the σ - component lies in the plane perpendicular to the plane of incidence of the crystal and the electric vector of the π - component lies in the plane of incidence. The intensity of the beam I can be expressed in terms of the intensities of the σ and π - components.

$$I = I_{\sigma} + I_{\pi}$$
(2.35)

For an unpolarised beam

$$I_{\sigma} = I_{\pi} = I/2$$
 (2.36)

If the 2-reflection system is aligned to the tolerances prescribed in Subsection 2.2.2, a geometrical analysis shows that, the power reflected from the face of Crystal B in either polarisation component, may be expressed in terms of $\ddagger \pm$ simple convolutions of the lines spread function thus:

$$P_{cc}(\beta) = S \int P(\theta)P(\beta + \theta)d\theta \qquad (2.37)$$

where S is a constant which is proportional to the intensity of the beam incident upon Crystal A. θ is the glancing angle of any ray onto Crystal A. β is the angular rotation of Crystal B from that position which satisfies the Bragg

[†]

In order to avoid obscuring the simplicity of relation (2.37) the geometrical analysis required to derive this expression is given in Appendix B. The lengthy three-dimensional trigonometry is required only to explore the effects of vertical divergence and horizontal divergence in the beam. This analysis is particularly relevant to the <u>shape</u> of the 2-reflection profile since this is more sensitive than is the <u>integral</u>, to these effects. Once the analysis is taken far enough to determine the limits within which these effects are negligible, then one will normally wish to have the simplicity of working within those limits.

[‡] Since the line spread function of Expression (2.37) is wavelength specific it should be written as P_{λ} but this explicit form has been omitted so as to avoid cumbersome expressions.

^{*} In the geometrical analysis of Appendix B the arguments of the line spread functions are referenced to the Bragg angle of the general ray in order to express the function arguments only in terms of the quantities under consideration. These quantities are no longer relevant to the present discussion thus it is convenient to express the arguments simply in terms of the glancing angle.

condition for the central ray so that ($\theta + \beta$) is the glancing angle of the general ray to Crystal B. The total power reflected from Crystal B is found by integrating over all rays to obtain $P_{cc}(\beta)$ which is the 2-reflection rocking curve. The 2-reflection integral R_{cc} is found by integrating $P_{cc}(\beta)$ with respect to β summing the integrals for the σ - and π - components

and normalising to the intensity of the beam incident upon Crystal B

$$R_{cc} = \int_{\beta_{1}}^{\beta_{2}} P_{cc}(\beta) d\beta = \frac{\int_{\beta_{2}}^{\beta_{1}} \left[S_{\sigma} \int_{-\infty}^{\infty} P_{\sigma}(\theta) P_{\sigma}(\beta + \theta) d\theta + S_{\pi} \int_{-\infty}^{\infty} P_{\pi}(\theta) P_{\pi}(\beta + \theta) d\theta \right] d\beta}{S_{\sigma} \int_{-\infty}^{\infty} P_{\sigma}(\theta) d\theta + S_{\pi} \int_{-\infty}^{\infty} P_{\pi}(\theta) d\theta}$$
(2.38)

The limits of the β - integration encompass the angular range of significant Bragg reflection at Crystal B. The line spread functions are finite only over a small angular range centred about their peak angles. Outside of this range $P_{cc}(\beta)$ will be zero and so the limits of the β -integration can be extended to \pm^{∞} without affecting the value of the integral. For an unpolarised beam incident upon Crystal A, from Eqn. (2.36), $S_{\sigma} = S_{\pi}$ and the S terms in Expression (2.38) cancel. This expression may now be written as $\int_{cc}^{\infty} \int_{-\infty}^{\infty} P_{\sigma}(\theta) P_{\sigma}(\beta + \theta) d\theta d\beta + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_{\pi}(\theta) P_{\pi}(\beta + \theta) d\theta d\beta$ (2.39) $R_{cc} = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_{\sigma}(\theta) d\theta + \int_{-\infty}^{\infty} P_{\pi}(\theta) d\theta}{\int_{-\infty}^{\infty} P_{\pi}(\theta) d\theta}$

The properties of convolution integrals as discussed in Appendix C allow (2.39)

to be considerably modified, yielding

$$R_{cc} = \frac{\left[\int_{-\infty}^{\infty} P_{\sigma}(\theta) d\theta \right]^{2} + \left[\int_{-\infty}^{\infty} P_{\pi}(\theta) d\theta \right]^{2}}{\int_{-\infty}^{\infty} P_{\sigma}(\theta) d\theta} + \int_{-\infty}^{\infty} P_{\pi}(\theta) d\theta} = \frac{R_{c\sigma}^{2} + R_{c\pi}}{R_{c\sigma}^{2} + R_{c\pi}}$$
(2.40)
where $R_{c\sigma}$ and $R_{c\pi}$ are the single crystal reflection integrals for pure

 σ -polarised and pure π -polarised beams. They are related to R_c for an unpolarised beam by the following expression

$$R_{o} = (R_{c\sigma} + R_{c\pi})/2$$
 (2.41)

 \mathbf{R}_{cc} can be expressed in terms of \mathbf{R}_{c} by introducing a polarisation ratio defined

$$k(\theta) = R_{c\pi}/R_{c\sigma}$$
(2.42)

Equation (2.40) becomes

$$R_{cc} = R_{c\sigma} (1 + k^2) / (1 + k)$$
(2.43)

Using Eqns. (2.41) and (2.42)

$$R_{cc} = 2R_{c} (1 + k^{2})/(1 + k)^{2}$$
(2.44)

The value of k is dependent in a complex manner upon such factors as absorption, extinction and crystal defect density and hence no general analytical expression for its calculation has been given. However, from Darwin theory (Ref ²¹, p.59) the values of k for two limiting cases may be obtained. For a perfect crystal with zero absorption $k = |\cos 2\theta|$ whilst for a mosaic crystal $k = \cos^2 2\theta$ If the pair of crystals used in the 2-reflection method can be identified with these limiting cases then

For Perfect Crystals with zero absorption

$$R_{c} = C_{p} R_{cc} = \frac{(1 + |\cos 2\theta|)^{2}}{2(1 + \cos^{2}2\theta)} R_{cc}$$
(2.45)

For Mosaic Crystals

$$R_{c} = C_{m}R_{cc} = \frac{(1 + \cos^{2}2\theta)^{2}}{2(1 + \cos^{4}2\theta)}R_{cc}$$
(2.46)

The correction functions C_p and C_m are plotted in Fig. 2.5a which shows that the correction applied to R_{cc} is a maximum at a 45^o glancing angle. The k values for real crystals normally lie between the values for the perfect and mosaic cases. If k is unknown for a pair of crystals then the uncertainty in the correction is large for glancing angles near to 35^o and 55^o. The worst case correction error at a given angle is incurred if C_m is used to correct R_{cc} under the assumption that the crystals are mosaic, when in fact, they are perfect, non-absorbing. The true R_c value will exceed the recorded R_c value by the factor C_p/C_m which is plotted in Fig. 2.5b. The figure shows that the error in the recorded R_c is as great as 32% near to 35^o and 55^o.

as



Figure 2.5a The relationship between the Bragg reflection and 2-reflection integrals as a function of Bragg angle for the two Darwin limits $k = |\cos 2\theta|$ and $k = \cos^2 2\theta$



Figure 2.5b The worst case error that may be incurred by use of the inappropriate Darwin correction in the calculation of Bragg reflection integrals from 2-reflection measurements

An additional source of uncertainty arises from the fact that in a few cases k values for real crystals have been reported which lie outside the range determined from Darwin theory. Jennings⁸⁴ observed a k value for a LiF mosaic monochromator which not only lay outside the limits but was in excess of $|\cos 2\theta|$. He explained the result in terms of a large secondary extinction.

Nevertheless the 2-reflection method in the (1, -1) parallel mode may be used to determine R_c accurately if the uncertainty in the correction to R_{cc} is small or if there is good evidence from other experiments about the nature of the crystal and the value of k.

ii. The (1, -1) asymmetric configuration. When Crystals A and B have different 2d values then for a (1, -1) reflection the crystal faces are not parallel. The total count E, obtained by scanning Crystal B through the region of significant Bragg reflection is

 $E = R_{ab} I_0 / \omega$ (2.47) where R_{ab} is the 2-reflection integral associated with the pair of crystals A and B. The desired quantity is R_b the reflection integral of Crystal B. The relationship between R_a and R_b can be derived by a simple line of argument as outlined below.

Consider an unpolarised beam incident upon Crystal A. If the horizontal beam spread function $h(\alpha)$ of this beam is broader than the Crystal A line spread function and is constant over the range of this function then the reflected intensity is proportional to R_a . The reflected beam is the incident beam for Crystal B, and the intensities $I_{0\sigma}$ and $I_{0\pi}$ in the σ - and π -components will be proportional to $R_{a\sigma}$ and $R_{a\pi}$ respectively. The following can therefore be written

$$I_{\sigma\pi} / I_{\sigma\sigma} = R_{a\pi} / R_{a\sigma} = k_{a\sigma}$$
(2.48)

$$I_{o} = I_{o\sigma} + I_{o\pi} = I_{o\sigma}(1 + k_{a})$$
 (2.49)

The total count reflected off Crystal B may also be resolved into σ - and π -

components to give

 \dagger

$$E = E_{\sigma}^{+} + E_{\pi}^{-} = (I_{\sigma\sigma}R_{b\sigma}^{+} + I_{\sigma}R_{b\pi}^{-})/\omega \qquad (2.50)$$
$$= I_{\sigma}(R_{b\sigma}^{-} + k_{a}R_{b\pi}^{-})/\omega$$
$$= I_{\sigma}(R_{b\sigma}^{-} + k_{a}R_{b\pi}^{-})/[(1 + k_{a})\omega]$$
$$= I_{\sigma}R_{b\sigma}(1 + k_{a}k_{b})/[(1 + k_{a})\omega]$$

Unless $k_a = 1$ the beam incident upon Crystal B is polarised but the required quantity R_b is the reflection integral for an unpolarised incident beam. Substitution for R_{ba} in (2.50) using (2.41), (2.42) gives

$$E = 2I_{o}R_{b}(1 + k_{a}k_{b}) / [(1 + k_{a})(1 + k_{b})\omega]$$
(2.51)

whence by comparison with (2.47) and using R_c as the generic term for the 1-reflection integral

$$R_{ab} = R_{c} 2(1 + k_{a} k_{b}) / [(1 + k_{a})(1 + k_{b})]$$
(2.52)

If the crystals are identical then clearly (2.52) reduces to (2.44) which was derived, using a geometrical approach, for this special case.

Equation (2.52) shows that if k_b is maintained constant by using a fixed test crystal and wavelength then as $k_a \neq 1$ so $R_{ab} \neq R_c$. It has been stated previously that from Darwin theory the value of k_a lies between the two limits $|\cos 2 \theta_A|$ and $\cos^2 2 \theta_A$. Clearly if θ_A is close to either zero or $\pi/2$

The geometrical approach which dealt with the (1, -1) parallel mode can be extended to embrace the asymmetric configuration mode in which the instrument is dispersive. For this case the λ -integral of the rocking curve cannot be separated out in the same way as for Expression (2.37) (see Appendix B) because the arguments of the line spread functions are λ dependent. This will also mean that the shape of the rocking curve is λ dependent. The expression equivalent to Expression (2.39) will contain a λ -integral but if the reflection integrals $R_{a\sigma,\pi}$ and $R_{b\sigma,\pi}$ are slow functions of λ then they become constants in the λ -integration which thus becomes trivial. The λ -integrals in the numerator and denominator cancel out and R_{\pm} is thus not affected by the λ -integration. By analogy to Expression (2.40) $R_{\pm} = (R_{\pm}R_{\pm} + R_{\pm}R_{\pm})/(R_{\pm} + R_{\pm}R_{\pm})$ and by substitution of polarisation ratios k_{\pm} and k_{\pm} an equation identical to Eqn. (2.52) is derived. It should be noted that Eqn. (2.48) is written for monochromatic beam but in the light of the preceding discussion the derivation of Eqn. (2.52) remains valid.

then k-1 regardless of whether the crystal is perfect or mosaic and the R_{ab} polarisation correction and its uncertainty will be small. The geometry of the Leicester instrument and of many others does not allow operation near $\pi/2$ but the small angle condition may be fulfilled by using a crystal with a large 2d. Evans et al.⁸³ applied the large 2d method to three test crystals ADP, KAP and PET. With each crystal they used a number of different mono-chromators and found that as the 2d of the monochromator increased so R_{ab} approached R_c obtained previously by a single reflection method.⁷⁹ Extrapolation to $\theta_A = 0$ in fact gave in each case an R_{ab} value which was in excellent agreement with R_c.

<u>iii. The orthogonal configuration</u>. This method derives its name from the fact that the rotational axes of the two crystals are orthogonal. It was devised to be used in conjunction with a conventional 2-crystal method in order to eliminate the polarisation correction. Suppose either R_{cc} or R_{ab} has been measured using the appropriate (1, -1) parallel mode or (1, -1) asymmetric configuration mode, the rotational axis of one of the crystals may now be rotated through $\pi/2$ about the direction of the test beam. In many instruments it is more convenient to adjust the axis of Crystal B and the following arguments apply to this situation.

As a result of the adjustment, the planes of dispersion of the two crystals are perpendicular and therefore a component of the test beam considered as π -polarised at Crystal A will be regarded as σ -polarised at Crystal B and vice versa. The integrated count for the reflected intensity from the Crystal B scan for such a configuration is

$$E^{\perp} = R_{ab}^{\perp} I_{o} / \omega$$
 (2.53)

where the superscript 1 refers to the orthogonal mode. Proceeding as for the (1, -1) non-parallel mode

$$I_{o} = I_{o\sigma} + I_{o\pi} = I_{o\sigma} (1 + k_{a})$$

$$E = E_{\pi}^{1} + E_{\sigma}^{1} = (I_{o\sigma}R_{b\pi} + I_{o\pi}R_{b\sigma})/\omega$$

$$= I_{o\sigma}(R_{b\pi} + k_{a}R_{b\sigma})/\omega$$

$$= I_{o}R_{b\sigma}(k_{b} + k_{a})/[(1 + k_{a})\omega]$$

$$= 2I_{o}R_{b}(k_{a} + k_{b})/[(1 + k_{a})(1 + k_{b})\omega]$$
(2.54)

whence, by comparison with Eqn. (2.53)

$$\mathbf{R}_{ab}^{I} = \mathbf{R}_{c} \ 2(\mathbf{k}_{a} + \mathbf{k}_{b}) / [(1 + \mathbf{k}_{a})(1 + \mathbf{k}_{b})]$$
(2.55)

If R_c was obtained from either R_{ab} or R_{ab}^1 then a polarisation correction would be necessary but this may be avoided, as shown by the following summation of R_{ab} and R_{ab}^1 $R_{ab} + R_{ab}^1 = 2R_c[(1 + k_a k_b) + (k_a + k_b)]/[(1 + k_a)(1 + k_b)]$ (2.56) $= 2R_c$

The R_c values obtained by averaging R_{ab} and R_{ab}^{1} measurements have been found ⁸³ to be in good agreement with values obtained by 1-reflection methods. c. Choice of favoured method

The 2-reflection methods that have been described enable R_c to be measured more efficiently than is possible using 1-reflection methods but at the expense of being compelled to take beam polarisation into account. The previous discussion shows that (1, -1) parallel measurements incur the largest errors due to uncertainties in the polarisation corrections. For a given Bragg angle these uncertainties can only be reduced if there is good evidence from other measurements (Ref. 81, p.104) or the crystal condition⁸⁵, as to appropriate polarisation ratios. The (1, -1) asymmetric configuration method, which is as efficient as the (1, -1) parallel method, minimises the polarisation correction uncertainties and indeed has proved itself to be useful for routine measurements. The method which combines the orthogonal mode with one of the other modes, eliminates the polarisation correction and is therefore not susceptible to correction errors. The results obtained are accurate but the method is rather slow in that two measurements are required and the alteration of the Crystal B rotational axis entails considerable adjustment of the instrument.

It was decided that the (1, -1) asymmetric configuration method should be implemented to measure the R_c values of the crystals studied in this work, especially as there is no difficulty in procuring monochromator crystals such as phthalates and stearates which are of larger 2d.

d. Sources of error and their containment

i. Alignment conditions. The following discussion considers measurements for which the rotational axes of the crystals are mutually parallel and the line of the axes defines the vertical direction. Details of the important points concerning instrument alignment for 2-crystal studies are given in Subsection 2.2.3 along with alignment tolerances.

The integrals R_{ab} and R_{cc} are slowly varying functions of rotational axis misalignment, crystal tilt and vertical beam misalignment, thus the respective alignment tolerances for rocking curve measurements can be relaxed by an order of magnitude for integrated reflectivity measurements.

It is important that the line of the test beam central ray passes through the rotational axis of Crystal B and that there is no crystal eccentricity. This will ensure that when R_c is measured for a number of wavelengths, the test beam will be incident upon the same area of the crystal surface for each Bragg angle and thus errors arising from R_c variations due to a non-uniform crystal surface will be eliminated. This will also apply to scans of larger angular range at small Bragg angles. Furthermore the detector is aligned as described in Chapter 3 and so both of these misalignments will cause a shift of the beam from the horizontal centre of the detector window (see Subsection 2.2.2.e).

The criterion governing the beam geometry is that the beam should be

contained within the surface area of Crystal B and the detector window. Plainly if part of the test beam, incident upon Crystal B, is lost to the detector, for example by 'spilling off' the end of the crystal, then the normalisation of the integrated count by the test beam intensity will be in error. The vertical and horizontal slits are required merely as aperture stops. It should be noted that the size of the reflecting area of Crystal B will change with the glancing angle. If the surface is non-uniform the horizontal aperture may require adjustment to ensure that the area size is constant for measurements at different wavelengths. Apart from this the slit settings are not critical. <u>ii. Measurement uncertainty on I₀</u>. The beam intensity and scan settings are optimised to give good counting statistics together with a reasonable scan duration. Further details are given in Subsection 3.4.3. The intensity of the test beam is measured before and after the scan to give I and I₀ respectively. The errors on these measurements are

$$\sigma I_{o_1} = \sqrt{C_{I_1}}/t_1'$$
 and $\sigma I_{o_2} = \sqrt{C_{I_2}}/t_2'$ (2.57)

where C_{I_n} is the integrated count of the beam intensity over the sample time t_n' . I_0 is the average of I_{01} and I_{02} and therefore from (2.21)

$$\sigma I_{o} = \left[\left(\sigma I_{o} / 2 \right)^{2} + \left(\sigma I_{o} / 2 \right)^{2} \right]^{\frac{1}{2}}$$
(2.58)

iii. Measurement uncertainty on E. The measured integrated count E_m of a rocking curve represents the sum of the wanted peak counts E and the background count E_B hence:

$$\mathbf{E} = \mathbf{E}_{\mathbf{m}} - \mathbf{E}_{\mathbf{B}} \tag{2.59}$$

The background count is measured in the following way. The background count rate is measured at two Crystal B positions referred to as 1 and 2. Both crystal positions are far removed from the peak position which lies midway between them. The average of the two count rates is multiplied by the scan time to give the background count. If I_{B_1} and I_{B_2} are the two measured background count rates then the associated errors are

$$\sigma I_{B_1} = \sqrt{C_{B_1}}/t_1'$$
 and $\sigma I_{B_2} = \sqrt{C_{B_2}}/t_2'$ (2.60)

where C_{B_n} is the integrated background count over the sample time t'_n at crystal position n. The errors in sample and scan times is negligible.

The error σI_B on the average background count rate I_B is determined by combining $\sigma I_{B1}/2$ and $\sigma I_{B2}/2$ using an expression analogous to (2.58). The error on the background count for the scan is

$$\sigma E_{B} = \sigma I_{B} t \qquad (2.61)$$

where t is the scan time.

The error on ${\rm E}_{\rm m}$ is calculated from the expression

$$\sigma E_{m} = \sqrt{E_{m}}$$
(2.62)

Finally σE_m and σE_B are combined by the method of probable errors to give σE .

iv. Measurement uncertainty on ω . The scan speed ω is measured using the following relationship

$$\omega = \Delta \theta / t \tag{2.63}$$

where $\Delta \theta$ is the angular range of the scan and t is the scan time. For scan ranges greater than about 2 arc minutes $\sigma \Delta \theta$ the error on $\Delta \theta$ is negligible and so the error on ω can be ignored. For short scans

$$\sigma\omega = \sigma\Delta\theta/t \tag{2.64}$$

v. Uncertainty due to polarisation. The polarisation correction C to a

2-reflection integral measurement is given from (2.52) by

$$C = [(1 + k_a)(1 + k_b)] / [2(1 + k_a k_b)]$$
(2.65)

From (2.26) and (2.65)

$$(\sigma C)^{2} = \left[\frac{1-k_{b}^{2}}{2(1+k_{a}k_{b})^{2}}\right]^{2} (\sigma k_{a})^{2} + \left[\frac{1-k_{a}^{2}}{2(1+k_{a}k_{b})^{2}}\right]^{2} (\sigma k_{b})^{2}$$
(2.66)

Equation (2.66) shows that for low glancing angles at Crystal A, σC is small

because σk_a the uncertainty in k_a is small and k_a is near to unity. If there is little evidence concerning the value of k then (Prins k value - $\cos^2 2\theta$)/2 may be used as a measure of σk .

e. Final measurement uncertainty on R_c

The measured quantities E, ω and I defined by Eqn. (2.47) are related to R by the familiar equation

$$R_{c} = CE \omega / I_{o}$$
(2.67)
where C is defined above. The uncertainties σC , σE , $\sigma \omega$ and σI_{o} are

combined using (2.21) to give the final measurement uncertainty on R_c .

2.2.2 Measurement of the function

The Bragg response, or line spread function $P_{\lambda}(\theta)$ is defined in Expression (2.5) in terms of an idealised beam incident on the crystal surface. An experimentally observed rocking curve consists of the profile of $P_{\lambda}(\theta)$ convolved with, other functions contributing to the instrument window function, and with the beam spectral function if the experimental mode is dispersive. Direct measurement of $P_{\lambda}(\theta)$ can only be achieved if experimental conditions are such that the associated convolution integral is dominated by the profile of $P_{\lambda}(\theta)$. The measurement methods described below were devised to fulfil these conditions.

a. The 1-reflection method. It is shown by Expression (2.28) that if $P_{\lambda}(\theta)$ is to dominate the experimental rocking curve then the widths of $G(\alpha, \psi)$ and $J(\lambda)$ must be small with respect to the width (w_c) of $P_{\lambda}(\theta)$. The crystal may be aligned and the incident beam collimated such that the effects of vertical divergence upon the rocking curve are negligible and so $G(\alpha, \psi)$ may be represented by $h(\alpha)$. Blake and Passin⁸⁶ introduced an experimental arrangement shown schematically in Figure 2.6. for which both $h(\alpha)$ and the effective $J(\lambda)$ are smaller than w_c . The horizontal beamspread of the


Figure 2.6 Schematic diagram of the 1-reflection fine slit method



Figure 2.7a Asymmetric cut Bragg reflection. The dashed lines indicate the angular width of the beam



Figure 2.7b Crystal configuration for the asymmetric cut method

incident beam is limited to $2\alpha_m^{<<}w_c$ by a pair of fine slits. The wavelength spread received at the detector is limited by a fine slit of width w<< Lw_c . If the spectrum of the emission line involved in the Bragg reflection is much broader than the line spread function then on rotation of either the detector or crystal, variations in the received reflected intensity will be due to $P_{\lambda}(\theta)$ only.

Definition of $P_{\lambda}(\theta)$, which improves as the slits are narrowed, is limited by the beam intensity losses which can be tolerated. A true definition of $P_{\lambda}(\theta)$ requiring infinitely narrow slits is clearly not realised. Nevertheless the method may be applied in the soft X-ray region, where w_c values are sufficiently large, to yield reasonable measurements of $P_{\lambda}(\theta)$. The method is in general limited by low intensities due to the small solid angle and bandwidth required by the method.

b. 2-reflection methods

i. Asymmetric cut method. If the diffraction planes of a crystal are not parallel to the surface then for the case of Bragg reflection θ_i and θ_r , the angles of the incident and reflected beams with respect to the crystal surface, will differ as shown in Fig. 2.7a. The dynamical theory of X-ray diffraction predicts for an asymmetric reflection that, if θ_i is smaller than θ_r the angular width of the beam and the angular range of reflection are contracted. This phenomenon may be expressed quantitatively by considering the angular range of total reflection from a lattice plane which is given by ^{87, 88}

 $w_{r} = (\sin \theta_{i} / \sin \theta_{r})^{\frac{1}{2}} w_{s}$ (2.68)

for the reflect beam. w_s is the angular range for a symmetric reflection. A similar expression will apply to the width of the line spread function of a real crystal. For a highly asymmetric reflection at glancing incidence, w_r will be appreciably smaller than w_s . This property of asymmetric reflections has been utilised by various workers ^{87,88} to obtain beams of low beamspread

which can be used to study the line spread function of another crystal. One particular experimental arrangement uses a 2-reflection parallel configuration as shown in Fig. 2.7b. Crystal A which is cut asymmetrically, is set for glancing incidence. Crystal B which reflects symmetrically is scanned to give a rocking curve. Equation (2.33) shows that in the parallel configuration the instrument is non-dispersive and so the rocking curve is independent of the beam spectrum.

The rocking curve differs fundamentally from the curve obtained from symmetrical reflection at both crystals for the latter is the convolution of the identical line spread functions of the crystals. In the asymmetric case, the width of the line spread function of the reflected beam from Crystal A is much less than the width obtained from symmetric reflection. Crystal A line spread function therefore has only a small influence upon the rocking curve which consequently will be dominated by the line spread function of Crystal B. In order to achieve this condition Crystal A must be cut such that $w_r/w_s = 0.2$. For a 45[°] Bragg angle this is achieved if the lattice planes are inclined 42.5[°] to the crystal surface so that $\theta_i = 2.5^°$. The intensities I_i and I_r of the primary and reflected beams respectively are related to θ_i and θ_r by the expression¹⁵

$$I_{r}/I_{i} = \sin \theta_{i}/\sin \theta_{r}$$
(2.69)

For the above conditions, (2.68) and (2.69) show that $I_r/I_i = 0.04$ and thus the method suffers severe intensity losses by comparison with the (1, -1) symmetric mode. For the latter mode typical beam intensities off Crystal B are 50c/sec. A typical count rate of approximately 2c/sec for the asymmetric mode would cause considerable counting statistic problems if the rocking curve were to be clearly defined. The method also suffers in that it is extremely expensive to cut crystals asymmetrically.

ii. A second approach to the problem is possible in the 2-reflection mode and it is this second approach which is exploited, perhaps for the first time, in this work. Discussion of this method is deferred to Subsection d. below so that the reader may compare this chosen approach with the complete list of options over which it is favoured.

c. 3-reflection methods

The reflection of a beam from two crystals in the dispersive (n, +n) position produces a beam which has a very small bandwidth and beamspread. This beam may be used to study the line spread function of a third crystal which can be set in either a plus or minus position. In order to minimise distortion of the rocking curve due to the monochromator crystals, the line spread functions of these crystals must be much narrower than that of the test crystal. This can be achieved by the following reflection techniques at the monochromator crystals:

- i. Asymmetric cut reflection.⁸⁹ The principles involved are described in Subsection 2.2.2.b.
- ii. High Order Reflection. Bubáková et al90 used this method to observe the line spread function of Ge(111) using three Ge(111) crystals in (3, 3, +1) configurations.
- iii. Use of monochromator crystals or another diffraction plane of the test crystal which have suitably narrower line spread functions. Bengtsson et al⁹¹ studied Ge(111) using quartz (1120) as monochromator crystals and clearly saw the asymmetry of the line spread function.

Technique ii. and normally technique iii. are limited to small wavelengths and Bragg angles, and so cannot be applied to the soft X-ray region. All three techniques incur large intensity losses because three reflections are involved and also the line spread functions of the monochromator crystals are narrow.

d. The presently chosen: (1, -1) method with theoretical modelling

In the preceding methods the approach has been to attempt direct measurement of $P_{\lambda}(\theta)$ with undesirable convolved components in the measured function contained within tolerable limits. Of course some further progress may be possible by solution for $\boldsymbol{P}_{\lambda}\left(\boldsymbol{\theta}\right)$ by deconvolution of the extraneous components, where these are known, by any of several numerical methods now well established. Indeed the power of these established computational methods is now such that, under certain special conditions, it may be possible to recover the desired function even if one of the extraneous functions is not, by comparison, a minor one. With this in mind consider the 2-reflection (1, -1) function given by Expression (B.8). Note that for proper machine settings and so forth the rocking curve under these conditions is defined solely by (the polarisation components of) $P_{1}(\theta)$. In this case therefore (neglecting for the moment considerations of polarisation) recovery of $P_{\lambda}(\theta)$ essentially requires only the recovery of $P_{\lambda}(\theta)$ from its own autocorrelation. Unfortunately as von Laue was the first to show,⁹² it is easy to see that it is impossible to perform this recovery directly and unambiguously without further This point can now be revealed in a most illustrative information. way by making the attempt to perform the deconvolution in Fourier transformed space. It will be immediately observed that a sign ambiguity occurs in taking the square root of every frequency component in the discrete Fourier transform of the data set. The inverse transform to arrive at $P_{\lambda}(\theta)$ is then clearly seen to be indeterminate. However, following von Laue's suggestion, suppose $P_{\lambda}(\theta)$ is postulated a priori, well-founded upon good Prins calculations, substantiated by good agreement with measurement of its integral (see Subsections 1.6, 2.2.1), and suppose this a priori prescription for $P_{\lambda}(\theta)$ is used to numerically predict the

2-reflection function, by evaluation of Expression (B.8). Then further suppose that the measured function proves to be identical with that predicted. Although, for the reasons given above, there can never be ultimate proof, this is, taking all things into account, persuasive evidence to believe that the original postulate for $P_{\lambda}(\theta)$ was correct and should be regarded as the line spread function for the analyser. Von Laue was prepared to go further and say that if the measured function differed, but only marginally, from that predicted then one might with justification, attempt modification to the postulated $\mathbf{P}_{\lambda}(\boldsymbol{\theta})$ and thus to iterate until the predicted curve is adequately consistent with that measured, and then to regard that final modified $P_{\lambda}(\theta)$ as the line spread function for the analyser. There is not much evidence that von Laue's suggestions have been implemented very frequently due perhaps to the great labour incurred in iterating through the numerical convolution of Expression (B. 8). However the general availability of fast computing machines now totally removes that difficulty. The remarkably precise agreement demonstrated throughout this work between measured and calculated values for the reflection integral (i.e. the integral of $P_{\lambda}(\theta)$) strongly suggests that the function $P_{\lambda}(\theta)$ may often be well determined by this method using only the simple 2-reflection (1, -1) method and without need of the greater difficulty and complexity of the methods discussed above. However in pursuing von Laue's suggestion, because of the difficulty in demonstrating the uniqueness of the result, it might be prudent to impose an additional condition namely that, during iteration, modifications to $P_{\lambda}(\theta)$ may be permitted only so as to model such conditions of the lattice as are believed to exist according to other information.

It is reasonable to modify $P_{\lambda}(\theta)$, as given by the Prins function, Expression (1.77), on the well-established basis that a real lattice contains 'holes' due to missing atoms, lattice displacements and contaminant atoms. The radiation scattered from such defect points is incoherent with respect to radiation scattered by other parts of the lattice and thus the total scattered beam suffers energy loss. This energy loss is equivalent to absorption and can therefore be modelled by introducing into the Prins function, an additional term which increases the calculated crystal absorption coefficient. Since the absorption coefficient μ_{g} is related to β (given by Expressions (1.69)) by (1.66a), this lattice condition may be modelled by multiplying β by the factor 1 + x. Recalling the above remarks we note that we shall permit this modelling only for such values of x as shall result in minor, and not gross, changes to $P_{\lambda}(\alpha)$. The model might be viewed as having 'first order perturbation' validity. We shall see later that under these conditions the technique has the general effect of reducing the computed P_{cc} values and has lesser effect on the w_{cc} values.

In the discussion of the zero-extinction model (see Section 1.6.1) the concept of a domain structure, as proposed by Darwin, 'was discussed. Experimental evidence shows that domain structure is a common imperfection of real crystals.⁹³ Clearly, for the near perfect crystals under consideration, the width of the domain orientation distribution function is narrow compared with that of the (extreme) ideal mosaic. Indeed it is shown in this study that this distribution function width will often be small with respect to the width of the Prins function. Nevertheless, since the domain structure lattice disorder tends to broaden the line spread function, it seems reasonable to model this effect by allowing each domain to be represented as having a line spread function $P_{\lambda}(\theta')$ and to allow the zero values of each of the set of θ' angle scales to be distributed with a Gaussian spread about the zero value of the θ scale. If we do this then our attempt to model the effects of the domain structure will in fact not change the extinction in the crystal as it really ought to do. However, if the f.whm of this spread to be modelled is small compared with the width of

 $P_{\lambda}(\theta)$ then the change in the extinction will be small and there is no serious error incurred in our neglect of modification of the extinction. In this respect it is again true that our modelling technique will only accurately describe analysers whose behaviour is a small perturbation from that of the perfect lattice. The technique will not be a good approximation if taken too far.

In the event, it was learned during the course of this work that the mosaic structure of the analysers used was such that no fit to the far wings of the measured (1, -1) rocking curve could be obtained by use of the above two techniques alone. In general the wings of the measured (1, -1) rocking curve were often much more extended than those of the self-convolution of the Prins function as modified by the above two techniques so optimised to produce a good fit to the peak and to the main body of the curve. This fact was one of the surprises of the work and the real origin of the effect is not understood. However, it seemed possible that a good fit to the wings might be obtained by supposing that a small fraction of the domains were members of a second population characterised by a very much larger Gaussian spread in their orientations. For such a population the modelling technique above would incur serious neglect of the change in extinction and therefore, on the face of things, is not an adequate way to describe their behaviour. However, generally only a very small fraction of the domains were members of this second population so that the overall effect of this neglect would then itself be small. Thus if the observed elevated wings are really due to such a second minority domain population, then inclusion of this second Gaussian spread, calculated without attention to the change in crystal extinction could therefore be expected to greatly improve the fit to the wings but would leave the computed reflection integral a little short of the proper value.

It should be noted that the first modelling technique models an energy

loss process (by increasing the effective value of μ_{g}) and therefore lowers the computed R_{c} whereas the Gaussian spreading technique, although based on the domain structure model, neglects to reduce secondary extinction and therefore has no effect upon R_{c} . The above modelling procedures were applied individually or in combination, in an iterative mode until agreement to within a few per cent was obtained between corresponding points on the computed and experimental (1, -1) rocking curves. Where wing studies of the (1, -1) rocking curve were made, agreement extending to 3 or 4 orders of magnitude down on P_{cc} was sought.

e. Sources of error and their containment

The principal source of error in the measurement of a (1, -1) rocking curve is curve distortion in the form of peak broadening and asymmetry. This distortion arises from geometric aberrations namely instrument misalignment and beam geometry. Unless otherwise stated, the procedures required to minimise sources of error are given in the discussion of error sources associated with the measurement of the Bragg dispersion function (Subsection 2.1.c.). Tolerances on the residual aberrations, which remain after minimisation (see Subsection 2.1.c.), must ensure that curve distortion is negligible in order that the observed (1, -1) rocking curve should arise purely from the crystal line spread functions. The tolerances should be such that the effect of peak broadening and asymmetry are within the limits of the measurement uncertainty of the (1, -1) rocking curve. Therefore peak broadening must contribute less than 2% to the curve fwhm and the asymmetry ratio r defined in Fig 3.12 b must be within the limits 0.99 < r < 1.01. Details of geometrical aberrations and associated tolerances are outlined below.

i. Diffractor settings

(1) Axes divergence from parallelity. The geometrical analysis for the

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1-crystal case (Subsection 2.1.c.) can be extended to the 2-crystal case if ϕ is now regarded as the angle between the two rotational axes. The effect of axial misalignment upon vertical misalignment is not relevant to the study of crystal line spread functions as is shown below.

In order that the crystal tilts remain aligned for rocking curves obtained over a range of Bragg angles it is necessary to limit the magnitude of 2ϕ to a small fraction of the residual tilt misalignment ($\sigma\delta$) tolerance. Details of the effect of tilt misalignment on a (1, -1) rocking curve are given below. Axes divergence is minimised by aligning both rotational axes to the local gravity vector as outlined in Subsection 3.3.3. A tolerance of 10" on the residual $\sigma\phi$ will satisfy the condition $2\sigma\phi<\sigma\delta$

(2) Mounting eccentricity. If Crystals A and B are displaced horizontally from their rotational axes by E_a and E_b respectively then the maximum shift of the beam along the surface of Crystal B for glancing angle θ is

$$S = 2 E_a \cot \theta + E_b \cot \theta$$
 (2.70)

The shape of the rocking curve is sensitive to the macrostructure of the crystal and so if the surface is non-uniform the beam shift S will cause differences in the curves obtained at various wavelength which cannot be accounted for in terms of changing wavelength. The width of the test beam measured along the surface of Crystal B is normally about 2 cms. Thus a maximum beam shift $\sigma\delta$ of 1 mm arising from the residuals σE_a and σE_b for the complete Bragg angle range, will give rise to a relatively small change in the effective nature of the crystal surface which contributes to reflection. In the residual eccentricity tolerance estimation put $\sigma E_a = \sigma E_b = \sigma E$. For a typical Bragg angle range of 5 - 65°_2 in order that $\sigma S < 1$ mm then $\sigma E < 30\mu$.

The maximum displacement of the beam reflected from Crystal B is given by

 $D = 2 E_a \cos \theta + 2 E_b \cos \theta$

(2.71)

It is important that D is as small as possible in order that non-uniformity in the detector window transmission does not affect the comparison of curves measured at different Bragg angles. For the above Bragg angle range and σE tolerance the maximum shift (σ D) of the reflected beam across the detector window is $< 70 \mu$. For a 1° scan rocking curve at $\theta = 44-45^{\circ}$, $\sigma D < 1.5 \mu$.

In the discussion of all alignment tolerances it is assumed that the detector is aligned as described in Chapter 3.

(3) Lattice tilts. Combined lattice tilts and vertical divergence give rise to peak broadening and peak intensity reduction, as is clearly illustrated in Fig. 3.12c. Schnopper⁹⁴ interpreted this as arising from a loss of resolution which in turn results from an increase in the instrumental window function width. For the (1, -1) parallel configuration this function may be written as

$$W(\beta) = \frac{1}{2} \sum_{p} \int g(\psi) \int P(v) P(\beta + v - \varepsilon_a + \varepsilon_b) dv d\psi \qquad (2.72)$$

where all terms are defined in Appendix B. Crystal tilts and vertical divergence give rise to negligible dispersion⁹⁴ and so peak broadening due to λ -dependence of the line spread function arguments will be small. Thus for the present discussion the line spread functions can be regarded as δ -functions (for both polarisations); Expression (2.72) then becomes

$$W(\beta) = B \int g(\psi) \int \delta(v) \delta(\beta + v - \varepsilon_a + \varepsilon_b) dv d\psi$$

$$= B \int g(\psi) \delta(\beta - \varepsilon_a + \varepsilon_b) d\psi$$
(2.73)

where B is a constant. Expression (2.73) is called the geometrical window function due to vertical divergence. Introduction of the full expressions for \approx_{a}^{a} and ϵ_{b}^{c} from Eqns. (B.2) and (B.3), using the approximation $n \approx \theta n$, gives

$$W(\beta) = B \int g(\psi) \delta\{\beta + \left[\frac{1}{2}(\delta_a^2 - \delta_b^2) \tan\theta_n - 2\delta_a^2 \tan\theta_n - 2\delta_a \delta_b \tan\theta_n\right] + \left((\delta_a + \delta_b)\psi/\cos\theta_n\right) d\psi$$

The terms in square brackets only affect the position of the geometrical window

function and may be ignored when considering the shape of the (1, -1) rocking curve. Thus Expression (2.74) becomes

$$W(\beta) = B \int g(\psi) \delta\{\beta + [(\delta_a + \delta_b)\psi/\cos\theta_n]\}d\psi \qquad (2.75)$$

The exact form of W(β) will depend upon $g(\psi)$ but its width w_g will be the width of $g(\psi)$ scaled by the factor $(\delta_a + \delta_b)/\cos \theta_n$. In order for the (1, -1) rocking curve to be the convolution of the crystal line spread functions only, the width of the geometrical window function must be zero. This is achieved when $\delta_a + \delta_b = 0$ i.e. when the crystal normals are parallel.

The crystal tilts need to be aligned such that either

i.
$$\begin{array}{c} \delta & = -\delta \\ a & b \end{array}$$
 or ii. $\begin{array}{c} \delta & = & \delta \\ b & \end{array} = 0$

The smallest (1, -1) rocking curve widths measured in this study are about 10" and thus it is reasonable to put an upper limit of 0.5" on w_g . It is now necessary to evaluate w_g for experimental conditions in order to estimate the necessary tolerance on the tilt residual that remains after tilt minimisation.

Figure 2.8a shows a pair of slits of heights 'a' and 'b' which define the vertical divergence of a beam incident upon Crystal A. ψ_{c+} , ψ_{c-} , ψ_{m+} and ψ_{m-} are defined with respect to the plane of dispersion XX'. If Ψ the beam misalignment is zero then $\psi_{c+} - \psi_{c-} - \psi_c$ and $\psi_{m+} - \psi_{m-} - \psi_m$. The target intensity is uniform in the vertical direction and so the angular intensity distribution $g(\psi)$ is constant for $|\psi| \leq \psi_c$ and decreases linearly with Ψ for $\psi_c < |\psi| \leq \psi_m$. $g(\psi)$ as a normalised function is given by ⁹⁵

$$g(\psi) = \begin{cases} 1/(\psi_{m} + \psi_{c}) & \text{for } |\psi| \leq \psi_{c} \\ (\psi_{m} - |\psi|)/(\psi_{m}^{2} - \psi_{c}^{2}) & \text{for } \psi_{c} < |\psi| \leq \psi_{m} \\ \psi_{c} = (b - a)/2L \text{ and } \psi_{m} = (b + a)/2L \end{cases}$$
(2.76)

The function $g(\psi)$ which is plotted in Figure 2.8b has a width $\psi_m + \psi_c$. The form of $g(\psi)$ given in (2.76) may be used in (2.75) to give

where



Figure 2.8a Side elevation of slits defining ψ , ψ_{c+} , ψ_{c-} , ψ_{m+} and ψ_{m-}



Figure 2.8b Angular intensity distribution $g\left(\psi\right)$ produced by Slits 1 and 2 in Figure 2.8a



Figure 2.8c Geometric window function $W(\beta)$ of the (1,-1) parallel position

$$W(\beta) = \begin{cases} (\psi_{\rm m} - \psi_{\rm c})B_{\rm l}/R & \text{for } |\beta| \leq R\psi_{\rm c} \\ (\psi_{\rm m} - |\beta/R|)B_{\rm l}/R & \text{for } R\psi_{\rm c} < |\beta| < R\psi_{\rm m} \end{cases}$$
(2.78)

where $B_1 = B/(\psi_m^2 - \psi_c^2)$ and $R = (\delta_a + \delta_b)/\cos \theta_n$ (2.79) Figure 2.8c shows a plot of W(β) for $B_1 = 1$. The width of the (1, -1) geometric window function calculated from (2.78) is

$$w_{gr} = R(\psi_{m} + \psi_{c})$$
 (2.80)

Substitution from (2.77) gives

$$w_{g} = R b/L$$
 (2.81)

In the interest of minimising w_g the second vertical slit is normally located between the crystals rather than before Crystal A. This choice of slit location is discussed in Paragraph iii. below. Equation (2.81) shows that w_g is dependent upon crystal tilts, the Bragg angle and the slit geometry and so all of these experimental factors must be taken into consideration when deciding upon the tolerance for the tilt residual $\sigma\delta$ (where $\sigma\delta = \sigma (\delta_a + \delta_b)$). For typical settings b = 4mm, L = 700 mm, $\theta = 45^{\circ}$, $\sigma\delta$ must be set at 1' to ensure $w_g < 0.5$ ".

Crystal misalignment normally introduces asymmetry into the (1, -1)rocking curve due to non-uniformity of the beam intensity distribution in the vertical plane. For simplicity assume a point X-ray source illuminating the first crystal. When the crystals are tilted each ray from the source will contribute its own (1, -1) curve at a slightly different setting of the spectrometer. If the intensity weighting of the rays is not uniform the net (1, -1)curve will show asymmetry. The effect disappears when the tilt error is zero since all contribution to the net (1, -1) curve occur at the same angular setting.⁹⁶ Figure 3.12cshows that for values of δ_b for which the condition $\delta_a + \delta_b = 0$ is nearly satisfied the peak is more sensitive to peak broadening than to asymmetry with changing δ_b and so the tolerances given above are sufficient to ensure negligible asymmetry. (4) Scan speed irregularities. The discussion given for the Bragg dispersion function (see Subsection 2.1.c.i.) is also appropriate to the measurement of the line spread function.

ii. Beam settings

(1) Horizontal beam misalignment. If the centre ray of the test beam does not pass through Crystal B rotational axis then the beam will strike different areas of the crystal as the Bragg angle is changed. The associated problems are described in Subsection 2.1. ii. The misalignments which cause the beam displacement are as follows:

(a) Error in the setting angles of Crystal A and the source. The instrument is aligned such that radiation of wavelength λ is reflected along the principal axis by Crystal A. In practice the crystal is set at $w_{a\lambda}$ by the angle scale using the principal axis as a reference line as shown in Fig. 2.9a. If the crystal is set at $w_{a\lambda}$ + ρ then for the same Bragg reflection the reflected beam will make an angle ρ with the principal axis. The test beam will be shifted along the face of Crystal B by

$$\mathcal{L} = \operatorname{R} \sin \rho / \sin \theta \qquad (2.82)$$

where R is the distance between the rotational axes (57cms). For the Bragg angle range 5 - 65° if $\rho < 0.6$ ' then the total shift of the beam $\Delta \ell < 1$ mm. The beam will strike the same area of the detector window regardless of θ_n . The distance between the horizontal centres of this area and of the window may be calculated from Eqn. (2.12) replacing $\sigma \chi$ by ρ . For the above tolerance on ρ ' this distance is 0.12 mm.

(b) Source focal spot misalignment. This misalignment is the distance x in the horizontal plane between the focal spot horizontal centre and the line which



(a) No Crystal A setting error



(b) Crystal A setting error ρ

Figure 2.9 The effect of error in Crystal A angle setting upon beam misalignment. RR', the principal axis, passes through the rotational axes. is both parallel to the incident beam and passes through Crystal A rotational axis. The shift of the beam along Crystal B surface is $x/\sin\theta$. For the above range of θ if x < 0.1 mm then the total beam shift is < 1mm. Again the receiving area of the detector window is independent of θ and the distance between the centre of this area and of the window centre is simply x.

(2) Horizontal divergence. In order to obtain an undistorted (1, -1) rocking curve it is required that the horizontal angular intensity distribution $h(\alpha)$ is constant over the region of observation. If this condition is not fulfilled then the convolution given by Expression (B.8) will be weighted by $h(\alpha)$. A narrow or non-uniform $h(\alpha)$ will also cause spectral distortion which may be shown mathematically by assuming $h(\alpha)$ to be a δ -function. Expression (B.7)

now becomes

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$$P_{cc}(\beta) = \iiint_{-\infty} P(v)P(\beta + v - \varepsilon_{a} + \varepsilon_{b})\delta(\varepsilon_{a} - z_{n} - v)g(\psi)J(\lambda)dvd\psid\lambda$$
$$= \iint_{-\infty} P(\varepsilon_{a} - z_{n})P(\beta - z_{n} + \varepsilon_{b})g(\psi)J(\lambda)d\psid\lambda \qquad (2.83)$$
Setting $\delta_{a} = \delta_{b} = 0$ and transforming variables

$$P_{cc}(\beta) = \int P(\gamma)P(\beta + \gamma)J \left(\lambda_{o} - \frac{\lambda_{o}\gamma}{\tan\theta_{no}}\right) d\gamma \frac{\lambda_{o}}{\tan\theta_{no}}$$
(2.84)

If the spectral distribution varies in the region that the convolution is non-zero then this will introduce spectral interference.⁹⁷

Distortion arising from both sources may be eliminated by using slits that are wider than the source focal region. This will ensure that $h(\alpha)$ is dominated by the slit transfer function rather than the focal region non-uniform intensity distribution. In the Leicester instrument the X-ray source is about 2.4 mm wide and may be regarded as a first slit. For a slit located between the source and Crystal A, $h(\alpha)$ has a form analogous to Expression (2.76). The widest and most uniform $h(\alpha)$ distribution is obtained if Slit 2, which is 26 cms from the source is set at 5.6 mm such that the beam width at Slit 3 is just less than 13mm, the maximum aperture of this slit. Providing the beam is contained within both crystal surfaces, then $h(\alpha)$ is reasonably constant over 42'. This is adequate for the crystals studied in this work, if the crystals are in reasonably good condition. If the mosaic model applies then the rocking curves may be very broad in which case distortion will arise. If the crystal surfaces are non-uniform the slit controlling horizontal divergence may need to be adjusted to ensure that the reflecting area size is the same for different wavelengths.

(3) Vertical beam misalignment. Vertical misalignment, defined in Subsection 2.1.c., alters the position but not the profile of the (1, -1) geometric window function. From Fig.2.8a and Subsection i. above, for a vertical misalignment $\Psi_{c_{\perp}} = \Psi_{c} + \Psi$, $\Psi_{c_{\perp}} = \Psi_{c} - \Psi$ (2.85)

Similar relationships hold for ψ_{m+} and ψ_{m-} . The expressions for $g(\psi)$ and $W(\beta)$ obtained for these conditions are identical to Expressions (2.76) and (2.78) respectively apart from the appropriate limits. Hence the (1, -1) rocking curve shape is independent of vertical beam misalignment.⁹⁴

(4) Vertical divergence. It is shown by Eqn. (2.80) that the vertical divergence of the beam will only affect the (1, -1) rocking curve shape if the crystal tilts are misaligned i.e. $\delta_a + \delta_b \neq 0$. In practice the slits controlling vertical divergence must be set according to the estimated tilt alignment uncertainty such that the geometrical window function width w_g is much smaller than the width of the self-convolved line spread function. The magnitude of w_g arising from typical slit settings and lattice tilt uncertainty is calculated in Subsection i. above from Eqn. (2.81).

iii. Discussion of slit locations

In a rigorous quantitative analysis, the horizontal and vertical divergence of the beam should be defined by slits located before Crystal A.

Consider firstly the vertical divergence slits; for any slit location other than the above, in the presence of misalignment, there will be vertical divergence in excess of that predicted from slit geometry alone. Nevertheless in order to reduce vertical divergence the second slit may be located either between the crystals or after Crystal B. Equation (2.77) may still be used to give a good approximation of the vertical divergence. For these alternative slit locations the vertical beam misalignment will depend upon the crystal tilts as well as the slit misalignment.⁶⁵ This will not affect the (1, -1) rocking curve shape which is shown in Subsection ii. above to be independent of vertical misalignment.

It is desirable for (1, -1) rocking curve studies that the horizontal divergence should be as large as possible and thus there is no need for the alternative slit locations. For the purpose of numerical analysis the beam should be collimated before Crystal A such that, the beam is contained within both crystal surfaces, and no other apertures affect the beam geometry.

f. Final measurement uncertainties

The measurement uncertainty on the (1, -1) rocking curve fwhm was estimated on the basis of the scan counting statistics. This uncertainty σw_{cc} was <u>+</u>1 sample bin width for the typical statistics given in Section 3.4. If the uncertainty in the counts in each sample bin is high then the correspondence between this uncertainty and distance on the abscissa axis was estimated and this was used to determine σw_{cc} .

The measurement uncertainty in the peak count rate (I_n) is given by

$$\sigma I_{p} = \frac{\sqrt{c}}{t}$$
(2.86)

where C is the total count in the bin or bins from which I_p is calculated and t is the time over which the count C was accumulated. The measurement uncertainty on P_{cc} is obtained by combining the uncertainties on the peak count rate and the incident beam intensity (see Subsection 2.2.1.d.) using the following expression

$$\sigma P_{cc} / P_{cc} = [(\sigma I_o / I_o)^2 + (\sigma I_p / I_p)^2]^{\frac{1}{2}}$$
(2.87)

Implementation of the (1, -1) method with theoretical modelling (working within the experimental limits prescribed above) provides a means of generating the Bragg analyser line spread function. Measurement of this function at wavelengths throughout the Bragg reflection wavelength range gives a family of line spread functions which give a complete quantitative description of the analyser.



Plate 3.1 General view of the Leicester 2-reflection instrument



Plate 3.2 General view of the Leicester 2-reflection instrument (with vacuum chamber lid removed) and the counting electronics



Plate 3.3 Plan view of the instrument in the (1, -1) position



Plate 3.4 General view of the instrument in the (1, -1) position

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CHAPTER 3

THE LEICESTER 2 - REFLECTION INSTRUMENT

3.1 Instrument Geometry

The demand ten years ago for routine calibration of crystals used in X-ray astronomy rocket experiments necessitated the construction of the Leicester 2-reflection instrument. It has a 2-axis geometry, based upon that employed by Parratt⁹⁸, and can be set to the (+n, -n) non-dispersive position thus enabling measurement of crystal diffraction characteristics.

General views of the instrument are shown in Plates 3.1-4. Simplified diagrams of the instrument are shown in Fig.3.1. The crystal turntables, source and detector are all contained within one vacuum chamber. Turntables A and B have fixed vertical axes and have independent rotational drive mechanisms. The source and detector rotate about the axes of Turntables A and B respectively and again have independent drive mechanisms.

The coarse rotation of crystals, source and detector is fully motorised and so the Bragg angular range $5-65^{\circ}$ may be studied during an evacuation period. This facilitates a rapid determination of the variation of crystal characteristics with wavelength. Fine rotation is achieved by tangent arm drives giving a scan range of 5° . This range is sufficient to accommodate even the broadest rocking curves such as those characteristic of mosaic crystals. The detector can be located to monitor the beam incident upon and reflected from Crystal B thus enabling the normalisation of the reflected beam necessary for reflection integral measurement.

The collimation of the instrument is shown schematically in Fig. 3. 2. All slit widths are adjustable both horizontally and vertically. The upper and lower dimensions above each slit are the maximum width and height



(a) Plan view

50cm



(b) Side elevation through XX' Source and detector located in the line XX'

Figure 3.1 Simplified diagrams of the Leicester 2-reflection instrument



Figure 3.3 Cross section through Turntable A assembly. Numbered parts refer to rings illustrated in Figure 3.8. Lettered parts are referred to in Subsections 3.2.2a, 3.3.1.

respectively. Dimensions of the source focal spot and detector window are also given. Reflection integral measurement only requires containment of the beam to Crystal B surface and the detector window and this is achieved easily by appropriate slit adjustment.

The generation of distortion-free (1, -1) rocking curves imposes tolerances upon crystal tilt alignment and further conditions upon beam collimation. The crystal mountings faciltate alignment to the tolerances given in Sections 2.1 and 2.2. Detailed description of the mountings and crystal alignment procedure is given in Sections 3.2 and 3.3 respectively. The beam must be collimated such that the horizontal divergence is much greater than the (1, -1) rocking curve fwhm. The maximum horizontal divergence of the slit system is 64 minutes of arc and so the necessary condition is satisfied for all crystals studied. In practice the horizontal slit widths had to be reduced in order to accommodate such factors as crystal length, Bragg angle and the need to use small areas of crystal surface for reflection. These factors are discussed in more detail in Chapter 2 and the chapters dealing with particular crystals. In spite of reduction, the horizontal divergence was still greater than the (1, -1) rocking curve fwhm in nearly all cases. The beam is also collimated vertically to minimise the effect of vertical divergence, discussed in Chapter 2. The large separation of 70 cms between Slits 1 and 3 gives the advantage as shown by Eqn. (2.81)of limiting vertical divergence distortion to a negligible level without the loss of beam intensity incurred if small slit settings had to be used.

Conversion to a 1-reflection instrument is readily achieved by removal of Crystal A and rotation of the source such that the beam passes through Crystal B rotational axis. The beam is collimated by Slits 1 and 3, the large separation of which provide adequate resolution for 2d determinations and absorption edge studies.

3.2.1 General features

A primary objective achieved in the instrument construction is the decoupling of the instrument proper from its vacuum envelope. This ensures no disturbance of the instrument alignment when the vacuum chamber is evacuated. Applying Deslattes⁹⁹ approach, the instrument and vacuum chamber are coupled 'independently to a third, rigid, structure in such a way that interaction between these primary elements can take place only through distortion of the third element.' The third structure is a concrete plinth sunk into the foundations of the building. The instrument base, of machine cast mehanite, is supported by three steel pillars embedded in the concrete plinth. The circular vacuum chamber base plate rests independently upon the concrete plinth and is sealed to the steel pillars by knife-edge seals.

The crystal turntables and the mounting block for tangent drive micrometers rest kinematically upon the instrument base plate which in turn is supported kinematically, thus allowing complete levelling adjustment.

The detector is fixed to a ring which is concentric with and attached to Turntable B assembly. The source is built upon a heavy arm which extends from a similar ring on Turntable A assembly. The source is a sealed vacuum unit which eliminates the need for a high chamber vacuum normally required for X-ray generation. A working chamber vacuum (10^{-2} mmHg) using a Welsh No 1398 "Duo-Seal" roughing pump, is thus achieved within minutes; an important factor in routine work which may involve changing crystals and slit settings several times during a working day. The roughing pump stands on the floor by the concrete plinth and evacuation is achieved through a port in the vacuum chamber base plate. Other ports in this base plate provide for electrical and water supplies, a vacuum release valve with chamber pressure monitoring using a Pirani Gauge (Edwards M6A). The steel lid of the vacuum chamber seals to the base plate by means of an 'O' ring along its rim. Perspex covered ports in the lid allow inspection of angle scales and moving parts.

3.2.2 Constructional details

a. Bearings The purpose-built precision bearing of each crystal turntable is shown for Turntable A assembly in Fig.3.3. A 2.5 inch diameter hardened steel shaft ^C, ground to better than 5 microinch roundness, runs in a preloaded journal which provides radial stability of the axis. The journal D, made of Flurosint has a low coefficient of sliding friction with hardened steel. The complete assembly of the turntable exerts no radial load on the bearing, thus there is no increase in friction with turntable load, and negligible wear on the journal bearing. The crystal table is mounted on a 7 inch diameter steel base plate E fixed perpendicularly to the steel shaft. Thrust bearing is provided by means of a 6 inch diameter aluminium-caged ball-bearing between the lapped faces of the steel plate and a steel ring fixed to race the main block of the turntable assembly (main thrust bearing plate F). Variations in ball-bearing size of about 5 microinch are averaged out by using a large number of ball-bearings resulting in a coning angle less than the measurement limit 0.1 second of arc. Coefficients of rolling friction are lower than coefficients of sliding friction and thus there is little increase in friction with the longitudinal load of the crystal table upon the bearing.

Relaxation of performance tolerances on the source and detector bearings is integral to their essentially identical construction. Concentricity of the source rotation about the Turntable A axis is achieved as follows. The turntable axis is aligned to the centre of the main thrust bearing plate. The source attachment ring locates about the rim of the bearing plate by means

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of three 120^o-spaced ball races one of which is spring-loaded. Thrust bearing is identical in type to that of the crystal tables.

b. Angle scales The angular setting of each crystal table is recorded by means of an engraved glass divided circle fixed to the base of the bearing shaft and centred about the rotational axis. An 11v 12w lamp housed in the vacuum chamber base plate illuminates the scale from beneath and a mirror-lens system projects the image of the 1 degree division graduated lines on to a frosted glass screen. The graduated lines are subdivided and the scale read by means of an optical micrometer which contains a 10 minute of arc division scale and two prisms, one of which has a 2 second of arc division scale engraved upon it. The angle between the prisms is adjustable, so allowing the alteration of the dispersion of the combined prisms required in the adjustment of the micrometer (see Subsection 3.3.2). The optical micrometers give a reading accuracy of 1 second of arc.

c. Crystal mountings Paramount to the design of the crystal mountings is the need to minimise crystal stress, resulting from location, so that perturbation of the lattice planes and the rocking curves is reduced. The fundamental feature of the crystal mountings (Fig. 3.4) consists of three adjustable ball-ended screws to which the surface plane of a mounted crystal is tangential. The balls enable alignment of the crystal planes to the plane parallel to and containing the turntable rotational axis. The lower ball is fixed to a remotely controlled micrometer spindle which facilitates vertical tilt adjustment during X-ray alignment. The crystal is normally mounted such that direct contact of the crystal surface with the balls is avoided because the pressure required to hold the crystal in place may cause surface damage or induce stress in the crystal. Most crystals supplied for study are mounted on to a metal substrate by means of a rubber adhesive which isolates the

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Figure 3.4 Crystal mountings - plan and side elevation



Figure 3.5 Crystal submount

crystal from stress in the substrate. The crystals are normally cut to a Philips block dimension (45 x 22mm). The vertical spacing of the balls is greater than the height of the block so that the latter can be fitted in an aluminium submount frame (Fig. 3.5) which makes direct contact with the balls. Adjustable beryllium-copper strip springs on the back of the submount hold the crystal surface lightly against three aluminium blocks which have faces coplanar with the locating face of the submount. The faces of the aluminium blocks are sufficiently large that stress due to location is much less than would result from a three-ball location. The submount locating face makes firm contact with the brass balls by means of three rods spring loaded against the back face.

<u>d. Source</u> Three important characteristics of the X-ray source (Fig. 3. 6) make it particularly useful in the measurement operation of the 2-reflection instrument. It is lightweight and easily mobilised by mounting it at the end of a rotating arm extending from Turntable A. The high radiation energy output (0.5 kilowatt) produces a beam reflected off Crystal B of sufficient intensity for good experimental counting statistics. The source vacuum is independent of the instrument vacuum chamber and for the reason outlined in Subsection 3.2.1 this makes for a rapid pump down cycle of the chamber.

The source anode and cathode operate at earth and negative H. T. and are housed in a hollowed 2.25 inch aluminium cube. The anode or X-ray target is a water-cooled cylindrical copper finger which may be rotated remotely by means of a gear wheel fitted to its base meshing with another gear wheel a sector of which is external to the aluminium cube. The cathode is a straight filament of 6 thou diameter tungsten wire aligned parallel to the target axis and located about 2mm away from the target surface. The target and filament assembly are each mounted on aluminium end plates which fitted



(a) Cross-sectional plan



(b) Source mountings

with 'O' ring seals, bolt against the sides of the aluminium cube.

Tungsten contamination of the target focal spot is reduced by locating the filament at the side of the target and focussing the electrons by a negative H. T. electrode. The electrode is simply a metal strip attached to a filament terminal and curved around the target. A window cut in the metal strip in front of the focal spot allows the X-rays generated to reach the source window. Henke and Tester¹⁰⁰ have constructed a source employing a more sophisticated electrode in order to place the filament on the opposite side of the target to the focal spot thus further reducing contamination. The rotational facility of the Leicester source allows uncontaminated areas of the target to be presented to the cathode without dismantling the source.

In much of the experimental work requiring excitation of emission lines the target was coated with a layer of fine powder consisting of a mixture of appropriate materials. The fine powder layer is formed by grinding the materials in a pestel and mortar, adding a few drops of a liquid (usually distilled water) to make a thin paste, painting this on the target and then drying the coating with the aid of a heat lamp. The coating applied is thin in order to avoid thermal and electrical insulation which produce unstable source operation.

Normally the target materials were compounds of the elements of the required lines as they are often more available and more suitable than the elements themselves. It is essential that the materials have high melting points (>700°C) in order to remain solid at the high temperatures of the target. Oxides were most commonly used but where an oxide was unsuitable it was found advisable in the interest of a high X-ray intensity to choose a compound in which the element is combined with atoms of small atomic weight. If a knowledge of the line wavelength is critical then the element

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or a compound with known chemical shift must be used.

The X-ray exit window is at the end of an aluminium channel machined from the same block as the aluminium cube. The source vacuum is isolated from the chamber vacuum by a thin transmitting plastic window supported at the rectangular aperture of the channel by a 1mm pitch grid. The thin window is clamped between an 'O' ring seal fitted to the end of the channel and a rectangular plate containing an aperture which bolts against the channel. Choice of window material depends upon the wavelength of the radiation to be studied. For $\lambda < 15$ Å aluminised melinex of 6 µm thickness is chosen whereas for $\lambda > 15$ Å stretched polypropylene of approximately 1µm thickness is used. The stretched polypropylene windows are extremely delicate and often do not survive more than one pump down cycle of the main chamber.

The source chamber connects, by means of another endplate containing a valve, to a vacuum line fitted to the main chamber roughing pump. A first stage rough vacuum is thus obtained. The source is provided with an ion pump (Ferranti FJD8) of 8 litre. \sec^{-1} pumping speed that connects to the source chamber by a steel pipe welded to a bolting plate. The ion-pump and roughing pump operate in conjunction to improve the rough vacuum. Once a pressure of about 10^{-4} Torr is achieved the ion-pump can take over completely from the roughing pump and the latter can be disconnected by closing the end plate valve whence an independent source vacuum (10^{-8} Torr) may be achieved.

The source and ion-pump bolt to a vertical aluminium plate which bolts against another vertical aluminium plate that is part of the source mounting table. Secondary location of the two plates in their interface plane is provided by adjusting screws which allow vertical and horizontal translational
alignment of the source in the plane tangential to the radial source arm. The source mounting table has a circular base that is mounted at the end of the source arm. The bolt holes in the base are machined such that the base location can be adjusted by rotation about a vertical axis which passes through the focal spot. The focal spot and window may thus be aligned with Turntable A rotational axis.

Two H. T. power supplies provide for high and low energy X-ray production. The output of these supplies are respectively 30kv - 13mA (Hartley Measurements Ltd. Model 421) and 5kv - 250mA (A. P. T. Electronic Industries Model 5705). The power supplies operate in conjunction with an emission stabilised A. C. filament supply unit (A. P. T. Electronic Industries Model 6246) which operates over the emission current range 0.4 - 270mA. The filament is connected to the power supplies by means of lead through connectors which emerge into an electrical junction box. In order to prevent electrical breakdown when the vacuum chamber is evacuated, the terminals in the junction box and the internal terminal in the spectrometer base are encapsulated in 'Sylgard' resin.

<u>e. Detector</u> The detector (shown in Fig. 3. 7) is a gas flow proportional counter chosen because of its high quantum efficiency, moderate energy resolution and negligible counting losses due to dead time effects.¹⁰¹ The main body of the detector is an earthed aluminium cyclinder of 2.5 inch diameter and 0.75 inch length. The anode is a high potential horizontal $50 \,\mu\text{m}$ diameter tungsten wire held diametrically by glass to metal seals in the walls of the detector body. The terminals of the seals external to the detector body are encapsulated in 'Sylgard' resin to prevent electrical breakdown in the vacuum. The resin is supported in aluminium arms which screw to the detector body.



Figure 3.7 Gas flow proportional counter

Crystal A and the other for the beam reflected off Crystal B. Each window is a 1 inch square aperture in a plate which screws to the open end of the detector body. A fine grid is placed over the internal side of the aperture with grid bars aligned 45⁰ to the vertical. Alignment of the bars parallel to the vertical causes modulation of the detector signal as the detector is moved across an X-ray beam due to interaction of the shadow patterns of the source window grid bars, the vertical edges of the collimating slits and the detector window grid bars. The grid supports an inner window of 1 µm stretched polypropylene that is clamped by a double 'O' ring seal between the plate and the detector body. It is essential that the windows are earthed in order to eliminate continuous discharge behaviour caused by charge build up at the windows due to low penetration soft X-rays. The internal sides of the windows are coated with a layer of graphite and earthed through the body of the detector. The graphite coating is applied by dipping stretched polypropylene in a 10% solution of Alcohol Dag in isopropanol. The graphite is washed from the external surface of the polypropylene which makes direct contact with the grid. The transmission ratio of the two windows over a required wavelength range are measured as described in Subsection 3.3.8 in order to make corrections to experimental results for differences in window transmission.

The detector and H. T. cable are insulated from the spectrometer in order to eliminate counter signal interference due to earth loops in the spectrometer metalwork. A perspex cover plate is used at the cable entry port and the detector is mounted on a perspex block which is screwed to a ring on Turntable B assembly.

The gas employed is a 90% Argon/10% Methane mixture at 1 atmosphere pressure which flows through the detector via an inlet and an outlet pipe in

the wall of the detector body.

The counter was tested by observing the pulse height spectrum of an Fe^{55} source. A typical spectrum for this counter is given in Ref.81. It was found that after several months of routine operation the resolution of the counter deteriorated. This was due to deposition on the anode wire of hydrocarbon polymers which could be removed by lightly brushing the wire with isopropanol.

f. Coarse drive system The four rotating elements of the instrument, i.e. crystal turntables A and B, the source and detector, can be located at any position within the angular ranges dictated by instrument geometry (see Section 3.1) by means of the coarse drive system. The coarse drive system for each turntable assembly is incorporated in a set of rings concentric about the turntable rotational axis. It may be described with the aid of Fig. 3.8 making special reference to Turntable A assembly. At the centre of the assembly is the crystal table which is rigidly fixed to the turntable bearing shaft. The table consists of a central crystal mounting platform (ring 1) and a ring which has gear teeth at its outer rim (ring 2). The crystal table is driven by a stepping motor and worm gear drive contained in the crystal drive ring (ring 3). This ring is maintained stationary by a radial arm extension which is spring-loaded against the crystal fine drive micrometer. Ring 3 also contains two spur gears which maintain the ring concentric about the crystal table. One of the spur gears is spring-loaded to ensure positive meshing between the crystal table gear teeth and the anti-backlash gear wheel of the drive ring gear box. The spring loading is adjusted by means of a grub screw which sets the position of a metal strip which impinges on the axial pin of the spur gear via a spring.

The design of the source coarse drive is the same in principle as that of the crystal drive. The source mounting arm is an extension of the source



Figure 3.8 Plan view of Turntable A assembly (schematic).



Figure 3.9 Principle of the detector and source position monitors (Turntable B system shown)

assembly ring (ring 4) which, like ring 2, has gear teeth at its outer rim. The drive motors and gears are contained in the source drive ring (ring 5) which is maintained stationary by means of a radial arm spring-loaded against the source fine drive micrometer.

Turntable B assembly differs only in that the detector is mounted directly on top of the detector assembly ring which is the counterpart of ring 4 described above.

g. Fine drive system Precision scanning of each rotating element is achieved by means of a tangent arm drive consisting essentially of a radial arm driven by a micrometer, the spindle of which is perpendicular to the arm. The tangent arm drives are shown in Fig. 3. 8 and are described in the following text with specific reference to the source and Crystal A drives. The fine drive micrometers are clamped in blocks which are supported on a large block mounted kinematically on the instrument base plate. Important features of the 1 inch traverse crystal micrometer include a non-rotating spindle and a large drum with a vernier readable to 1×10^{-5} inch. The micrometer is driven by an I. M. C. step servo motor and two precision speed reduction gear boxes.

The crystal radial arm engages with the micrometer spindle by means of spring-loaded contact between a hardened stainless steel plate screwed to the end of the radial arm and a steel ball attached to a block which clamps the spindle. The ball is fixed to an adjusting screw thus allowing adjustment of the tangent drive radius. Side 'play' of the micrometer spindle in its collar causes irregularities in angle generation of several seconds of arc and is eliminated by attaching a spring between the base of the radial arm and the block clamped to the spindle.

Tolerances on the crystal tangent drive movement may be relaxed for

the source/detector tangent drive movement (see Subsection 2.1.c). The source fine drive employs a 2 inch traverse micrometer with a rotating spindle and a vernier readable to 1×10^{-4} inch. The end of the spindle makes direct spring-loaded contact with a steel ball at the end of the source drive ring radial arm. The steel ball, as in the crystal tangent drive, is attached to an adjusting screw so allowing adjustment of the radial arm length. The tangent arm drives for Crystal B and the detector are identical to those of Crystal A and the source respectively.

The 2.1 velocity ratio of the detector and Crystal B scan and also the source and Crystal A scan is obtained by a combination of feeding the pulse generator signal to the micrometer motors, through a divider circuit and by using appropriate gearboxes between the motor and micrometer. The adjustable steel balls allow final adjustment of the 2.1 ratio and also the 1:1 ratio required when scanning the crystals simultaneously. Since the motors are powered by a common pulse generator the ratios are maintained at all possible scan velocities.

h. Detector and source position monitors The location of the source and detector at the 20 settings is monitored by a simple optical system shown schematically in Fig. 3.9. Infra-red radiation from an emitting diode is reflected off a mirror mounted below the crystal and then off a mirror mounted at the base of the source or detector. The latter mirror is aligned such that, at the 20 position, the beam is reflected back along the same path and some of the radiation is transmitted, through the 45° plate, to quadrant photocell. The photocell signal is fed to a differential amplifier and then to a simple ammeter. A broad response profile may be obtained by scanning the detector or source through the 20 position. The quadrants of the photocell are connected such that in the centre of the profile the signals from the two pairs of quadrants are nearly equal. This produces a sharp dip at the centre of the

profile which gives a location sensitivity of about 2 minutes of arc.

The location of the detector, when set to receive the beam reflected off Crystal A (referred to as the detector I_0 position), must also be monitored. For this purpose a mirror is mounted on the detector base on the side opposite to that of the 20 location mirror.

<u>i. Collimation</u> The instrument is provided with three pairs of slits. Each pair consists of two sets of brass jaws which determine the horizontal and vertical divergence of the beam. The slits open symmetrically about a centre line by means of a screw and spring mechanism. It should be noted by future operators that the slits do not close symmetrically about the centre line and that future slit designs should eliminate this fault. Each pair of slits is mounted in a block which is held in position by adjusting screws thus allowing vertical and horizontal translational adjustment and alignment of the slit centre lines parallel to the rotational axes and the plane of dispersion.

Two pairs of slits (Slits 1 and 2) collimate the beam incident upon Crystal A and these are mounted at the ends of the collimator assembly immediately in front of the source. The collimator assembly, built on a platform extending from the source mounting block, has provision for mounting a Soller collimator which in the present work was only used in the optical alignment of the instrument.

A third pair of slits (Slit 3) is mounted between the crystals on a screening shield, a curved aluminium plate which screens stray radiation from the detector. This pair of slits acts as a field stop aperture and may also be used in conjunction with Slit 1 to provide longer base-line beam collimation than that of Slits 1 and 2. This allows larger slit apertures for a given beam divergence.

j. Filters A twelve position aluminium disc filter wheel, fitted to the

platform of the collimator assembly intercepts the beam after Slit 2. The disc is furnished with removable aluminium plates to which the filters are attached. The wheel is rotated remotely by means of a twelve position Ledex switch.

3.2.3 Counting electronics

A block diagram of the counting electronics is shown in Fig. 3.10. Most units form part of a N.I.M. system which facilitates rapid change of modules and addition of further modules. The detector is powered by a 0 - 3kv high voltage power supply (Ortec Model 456) operating in positive polarity. The detector signal is fed to a pre-amplifier (E.G. & G. University Series Model 249) all components of which are rated to 3.0kv. The preamplifier is fitted with an open circuit/short circuit switch to protect the transistors during switching on and off the detector H.T. or the vacuum chamber roughing pump if the detector H.T. is on. The pre-amplifier output is fed to the main amplifier (Ortec Model 485) which also contains the power supply for the pre-amplifier. The amplifier output is fed to a single channel pulse height analyser (Ortec Model 406A) which determines by discriminator gates the energy passband to the counting units. The amplifier output is displayed on a multichannel pulse height analyser (Northern Scientific NS600) and a cathode ray oscilloscope (Telequipment Model D67).

The analogue ratemeter (Ortec Model 449-2) is fitted with audio output and logarithmic/linear output to a chart recorder. The latter facility was not employed due to indistinct separation of sampling bins typical of analogue output. Logarithmic/linear output to the chart recorder is provided by a four figure display digital ratemeter (Nuclear Enterprises Model 4622). The ratemeter sample time settings is altered in steps which were often too coarse and so in the latter part of the work the ratemeter was coupled with a clock



Figure 3.10 Counting electronics - block diagram



Figure 3.11 Plan of the instrument indicating the kinematic location mounting feet. Location of the Talyvel during rotational axis alignment is also shown.

(Nuclear Enterprises Model 4624) which enabled finer adjustment of the sample time. The timer (Ortec Model 773) and counter (Ortec Model 775) both have six figure digital display and are coupled such that the duration of the counter operation is slave to the timer which may operate for a pre-set time or infinity. The final display of the detector output is on a multi-speed, multi-response range chart recorder (Esterline Angus Servo Speed). A potentiometer (Beckman Helipot) provides fine adjustment of the pen response.

The complete counting system is tested and adjusted by switching off the detector and feeding into the pre-amplifier the signal from a tail pulse generator (BNC Model BH-1).

3.3 Adjustment and Alignment

3.3.1 Bearings

Coarse adjustment of radial location of each bearing shaft was achieved by four 90° -spaced horizontal screws G (see Fig.3.3) which screwed into the main thrust bearing plate and impinged on the outer walls of the split journal bearing assembly. The detector or source drive ring was removed in order to gain access to these screws. Three 120° -spaced vertical screws H which fix the split journal bearing to the turntable assembly provided fine adjustment of radial location. Access to these screws as to all other screws in the split journal bearing was gained by holes J in the turntable baseplate E.

Eccentricity of the turntable to the main thrust bearing plate was measured and adjusted accordingly by mounting a mitronic on the turntable baseplate such that the mitronic arm was in line with the diameter of the turntable. The mitronic needle rested against the outer rim of the main thrust bearing plate and so any eccentricity of the turntable gave rise, as the turntable rotated freely, to needle deflection which was accurately monitored. The ranges of needle deflection for complete revolutions of Turntables A and B were 1×10^{-3} inch and 5×10^{-4} inch respectively.

Clearance between the split journal bearing and the bearing shaft was adjusted in the following way. Three 120° - spaced screws K (see Fig. 3. 3) which attach the split ring to a mounting ring L were loosened. Screw M (see Fig. 3. 3) which varies the ring splitting was adjusted to give the required clearance and the three screws were tightened again. Screw M was also used for fine adjustment of clearance. Sideplay in the turntable bearing was measured using a mitronic in the following manner. The bearing was locked by maintaining the crystal drive stationary. The mitronic stand was clamped to any stationary part of the instrument and the mitronic needle was located against the rim of the crystal turntable. Finger pressure was applied to the diametrically opposite rim and sideplay was measured by noting any difference in the needle position before and after the pressure was applied. These measurements were repeated at several other points on the rim of each turntable. The maximum sideplay for each turntable bearing was 3×10^{-6} inch.

Sideplay tolerances on the source or detector mounting rings are not as critical as for the crystal turntables and so the spring-loaded ball race (see Subsection 3.2.2.a) was adjusted until any sideplay detectable by hand was eliminated. The ball race loading was adjusted by means of a grub screw, access to which is gained from the side of the turntable assembly.

3.3.2 Angle scales

The divided circle and optics of each angle scale can only be adjusted from below the turntable assembly and so each assembly was in turn mounted on to a purpose built steel frame. The divided circle is furnished with screws which adjust its concentricity about the bearing shaft but this adjustment was unnecessary in this work. The mirror-lens system was adjusted such that the projected area of illuminated scale was central and square on the viewing screen and the engraved scale lines were focussed at the plane of the 2 second of arc vernier scale. The 10 minute of arc division vernier scale was adjusted so that two adjacent lines on the engraved scale were projected on to the 0 and 60 minute of arc marks of the vernier scale. The angle between the two prisms in the optical micrometer was adjusted so that when the 2 second of arc division vernier scale was moved through its complete range (10 minutes of arc) the projected engraved line appeared to move 10 minutes of arc on the 10 minutes of arc division scale. Movement of the illuminating lamp slightly disturbs the projection of the engraved lines and from time to time the lamp position had to be checked and adjusted as necessary.

In the present study the determination of d_{α} and $\Delta \theta(\lambda)$ required the calibration of Turntable B angle scale. The calibration involved rotation of the turntable through a given angle and comparison of angle scale measurement of this angle with that of an independent method. This method entailed mounting an angle block, of accurately known angle, on the turntable, obtaining an autocollimator reflection from a face adjacent to the angle and then rotating the angle scale through the angle, calculated to give a reflection from the other adjacent face of the block. If the true angle generated is different from the angle apparent from the angle scale then the reflected beam will be displaced from the incident beam. This displacement was measured by the autocollimator so calibrating the angle scale for the particular angle generated.

The angle blocks consist of hardened steel combination angle gauges rung together to give the required angle. The angle of each gauge is determined to an accuracy of ± 1.0 second of arc. For each wavelength involved in the determination, the angle block was made up to 2θ and the turntable was rotated from and to the experimental angle scale settings. The

angle block was in fact made up to the nearest degree so using fewer angle gauges than required for the exact 20, thus limiting the uncertainty on the angle block. A block of small linear dimensions is also less cumbersome than a large block and is easily clamped to the turntable thus reducing the probability of block movement during turntable rotation. No more than 5 gauges were required in any angle block. Since the block is made up to the nearest degree the micrometer vernier settings will be the same at the two reflection positions and therefore uncertainties due to maladjustment of the verniers will be eliminated in 'the angle scale calibration. The maximum discrepancy between the true and apparent angle generated was approximately 20 seconds of arc.

3.3.3 Turntable axes and crystals

The turntable axes were aligned mutually parallel by independent adjustment of each axis to the local gravity vector using a Talyvel, an electrical levelling device sensitive to inclination changes of 0.1 second of arc. The instrument baseplate was levelled approximately by locating the Talyvel head on the polished baseplate of one turntable, parallel to the line of the mounting feet A and C (see Fig. 3.11) and then, without rotating the turntable, locating the Talyvel perpendicular to this line. This was repeated for the other turntable settings noting the Talyvel readings throughout. The whole procedure was repeated for other turntable settings until the trend in the Talyvel readings showed the general tilt of the instrument. The instrument baseplate was aligned by adjusting the mounting feet A, B and C.

Each turntable axis was aligned parallel to gravity by clamping the Talyvel head to the turntable baseplate and rotating the turntable by hand through a complete revolution. If the axis is not parallel to gravity the Talyvel reading will vary sinusoidally with an amplitude corresponding to the

axis offset angle. The mounting feet E, F and H, I of turntable assemblies A and B respectively were adjusted to reduce the Talyvel reading variations to a minimum. The axis were aligned parallel to gravity to within 0.3 second of arc and mutually parallel to within 0.6 second of arc.

The manufacturer's tolerance on the angle between the crystal surface and the lattice planes is 2 minutes of arc consequently, if the crystal surface is optically aligned such that it is parallel to and contains the rotational axis, the latter alignment will be disturbed negligibly by X-ray alignment of the lattice plane tilts. The ball-ended screws which define the crystal surface plane were adjusted in the following way. The position of the rotational axis in the horizontal plane was located by means of a travelling microscope which had two-directional translation in the horizontal plane. A card with a fine cross cut into it was lightly fixed on to the turntable and whilst viewing the cross through the microscope, the turntable was rotated by hand and card moved in a reiterative manner until the centre of the cross remained stationary as the turntable rotated. The microscope cross-hairs were aligned to the centre of the cross which was now in line with the rotational axis. The card was removed and the cross-hairs acted as a reference for locating the position of the rotational axis in further alignment.

A rectangular glass plate (supplied by Ealing Optical Works Ltd) with faces parallel to 1 second of arc and aluminium-coated on one side was lightly clamped in the crystal mountings with the mirror face, which assumed the crystal surface plane, making direct contact with the ball-ended screws. These screws were adjusted to align the glass block approximately to the vertical and the top edge of the mirror face to the microscope cross-hairs. An autocollimator was also set up to obtain a reflection off the mirror face and then after a turntable rotation of 180[°] off the back of the mirror face. The tilt micrometer and autocollimator were adjusted until the reflected beams off the front and back of the mirror face were coincident in height with the incident beam thus locating the face parallel to the rotational axis.

The two alignment procedures required to align the mirror to the microscope cross-hairs and the autocollimator are interdependent in the sense that adjusting the screws to satisfy one alignment condition disturbs their settings satisfying the other alignment condition. Consequently the alignments were repeated in conjunction with one another until both conditions were satisfied. The accuracies of the tilt alignment and centralisation to the rotational axis were 1.0 second of arc and 20 micron respectively. The alignment procedures were repeated, without moving the autocollimator, for the other turntable. The autocollimator settings required for alignment of both turntables differed by 0.6 second of arc thus confirming the accuracy of the rotational axes alignment.

It should be noted that the mirror tilt altered when the sprung clamping rods were overtightened. It is essential that the mirror (or crystal submount) is lightly clamped and the three clamping rods make positive contact and exert equal pressure.

The crystal diffraction planes are in general not precisely parallel to the crystal surface and therefore had to be aligned by an X-ray alignment method⁹⁴ which is described below with the aid of Fig. 3.12. Crystals A and B were set in the (1, -1) configuration with the tilt micrometers set to the nominal optical zero tilt setting. A series of rocking curves was generated over a range of Crystal B tilt micrometer settings to determine the optimum setting at which w_{cc} and P_{cc} simultaneously had minimum and maximum values respectively and the asymmetry ratio was unity. At this optimum setting the diffraction planes of Crystals A and B were parallel and therefore







Figure 3.12b Curve parameters used during X-ray alignment



Figure 3.12c X-ray alignment data for EDdT (020) at 4.85 Å. Optimum tilt setting indicated by dashed line.

with respect to the (1,-1) rocking curve profile studies for which peak position is not important no further alignment was required (see Subsection 2.2.2). For single and double crystal dispersion mode studies the diffraction planes must also be parallel to the rotational axes. Crystal B and its submount frame were then rotated through 180^o about the axis normal to the crystal surface and by the above procedure the optimum tilt micrometer setting was determined. Figure 3.12a shows that the difference between the two optimum tilt micrometer settings is twice the tilt error of Crystal A. Appropriate tilt adjustments were made to Crystals A and B to align their diffracting planes parallel to their respective rotational axes. Removal of Crystal A converted the instrument into a single crystal spectrometer for which the crystal is correctly aligned. The diffraction planes were aligned to an accuracy of $-\pm 3$ minute of arc. It was found that for crystals supplied by Quartz and Silice the optimum tilt settings were only a few arc minutes from the optical zero tilt settings and therefore the single crystal alignment tolerances (see Section 2.1) were satisfied merely by inserting the crystal and submounts with the tilt micrometer at the optical zero tilt setting.

3.3.4 Slits

The slits defining horizontal divergence were aligned in the following manner. The cross-hairs of a travelling microscope were set on a vertical 60µm diameter wire stretched across a groove in the locating face of an empty crystal submount mounted on Turntable A. The turntable was rotated by hand and the submount was adjusted within the location plane until the whole wire appeared stationary as it rotated and was thus aligned to the rotational axis. The centres of Slits 1 and 2 were aligned, using the travelling microscope, to the line parallel to and midway between the walls of the collimator assembly. A light beam, defined by the slits set to 0.1 mm, projected on to a translucent film (Kodak), an image of the wire which was viewed from behind the translucent film by a travelling microscope. The source mounting block to which the collimator assembly is fixed was rotated about a vertical axis to align the light beam symmetrically in the horizontal plane about the wire.

The alignment method for Slit 3, similar in principle to that for Slits 1 and 2, involved clamping an aluminium block, containing an axis slit of 9 minutes of arc divergence, in the crystal mountings of Turntable B. The slit block design facilitated symmetrical location of the slit about the plane tangential to the ball-ended screws and hence about the rotational axis also. A light source was placed behind the axis slit and with Slit 3 open the turntable was set such that the beam was symmetrical about the wire on Turntable A. The wire image was again viewed by means of the translucent film and travelling microscope as described for Slits 1 and 2 alignment. Slit 3 location was adjusted to the position at which the image of the slit opened symmetrically about the wire image as the slit was opened. The accuracy of slit image centralisation about the wire image was $\pm 10 \ \mu m$.

In the above alignment Turntable B was set at the zero Bragg angle setting and therefore switching the wire and axis slit gave this setting for Turntable A. Turntable zero Bragg angle settings were determined to an accuracy of + 5 minutes of arc.

Alignment of the slits defining vertical divergence to the plane of dispersion was accomplished by setting the slits to the same height using a

[†] Turntable B assembly and the fine drive micrometer support table must be aligned (see Subsections 3.3.3, 3.3.6) prior to the alignment of Slit 3 as the screening shield which supports Slit 3 is screwed to these. The shield must be located such that Slit 3 position is rigidly fixed, with no disturbance of or stress induced in the kinematic location of the turntable assembly and the support table.

vertical traverse travelling microscope. This necessitated alignment of the optical axis of the microscope to the plane of dispersion because the instrument construction dictated a different distance between the microscope and each slit. The microscope alignment involved clamping an 18 inch bar horizontally and centrally to Turntable A crystal mountings. The turntable was set to align the bar roughly colinear with the microscope barrel which pointed approximately along the line joining the turntable centres. The microscope was mounted on an adjusted levelling table and focussed with no parallax on the end of a horizontal pin attached perpendicularly to one end of the bar. The turntable was rotated through 180[°] and the cross-hairs were reset on the pinpoint. Any apparent difference in the height of the pin was due to offset of the optical axis from the plane of dispersion since the locus of the pin is in this plane. The height and inclination of the microscope barrel were adjusted reiteratively until the height discrepancy was eliminated.

The microscope barrel height was then adjusted to set the cross-hairs at the mid-height of the ball-ended locating screws of the crystal mountings. The centre of each slit was then aligned to the cross-hairs to an accuracy of ± 0.1 mm. The slit settings were checked by shining a light through Slits 1 and 2 which were set to small apertures and checking that the beam was symmetrical about the centre of Slit 3.

The aligned microscope was used to check that the source and detector move in the plane of dispersion by observing that they maintained the same height throughout their rotation ranges.

3.3.5 Source and detector position monitors

The source position monitor was aligned by inserting a mirror in Turntable A crystal mountings and setting the turntable and source arm to reflect a narrow beam defined by Slits 1 and 2 on to the horizontal centre of Slit 3. All slits were previously aligned as described in Subsection 3.3.4. The monitor mirror on the source drive ring was then adjusted to set the meter needle to the dip position. A second mirror was mounted on Turntable B to reflect the beam on to the detector window. The illuminated area of the window was viewed from behind the detector which was positioned such that the area was central and the windows were perpendicular to the beam. The operative monitor mirror at the base of the detector was adjusted as described above. The detector was then set behind Slit 3 and the other mirror on the detector base was adjusted. The accuracy of the mirror alignments was ± 2 minutes of arc in terms of source or detector movement.

3.3.6 Coarse and fine drives

The loading of the spur gears of each coarse drive ring must not be so high as to impede the coarse drive movement but must be sufficient to eliminate play in the drive ring location in order to maintain the effective length of the radial arm constant and prevent slipping when the fine drive is in operation. The loading for each crystal drive ring is particularly critical, and adjustment involved noting the turntable angles generated by consecutive, equal movements of the fine drive micrometer. The loading was increased until the generated angles (3 minutes of arc) were equal to within the angle scale reading error. It should be noted that for all fine drive scanning in alignment and experiment, the coarse and fine drive backlash were removed over 10 degrees and 10 minutes of arc respectively.

The fine drive micrometer support table shown in Fig. 3.11 was aligned by placing a Talyvel on the table surface and adjusting the mounting feet X, Y and Z. The table base was lightly clamped, without disturbing the Talyvel

reading, to the instrument baseplate by screw S and a sprung washer. Each fine drive micrometer was aligned such that at the midpoint of the traverse range the spindle was perpendicular to the radial arm. Each micrometer was clamped about the spindle collar in a heavy block screwed to the support table. The clamping was sufficient merely to hold the micrometer firmly in position since excessive clamping distorted the collars and impeded the spindle movement.

The effect of spindle sideplay of the crystal fine drive micrometers was demonstrated by using the complete micrometer traverse to generate consecutive 1 degree angles and noting the micrometer scale intervals. Irregularities in the micrometer scale intervals were equivalent to as much as 10 seconds of arc turntable rotation. The micrometer scale intervals required to generate 1 degree angles should be smaller at the centre of the micrometer traverse than at the extremities as a result of the tangent drive but this trend was not obvious.[†]

The fine drive speed ratios were set by fine adjustment of the lengths of the radial arms. The ratio of either the source - Turntable A or detector -Turntable B was adjusted before the Turntable A - Turntable B ratio in order to preset the source or detector radial arm length such that the ball-bearing determining this length located against the end of the micrometer spindle throughout the micrometer traverse range. The following sequence was adopted for the ratio adjustments:

- a. detector-Turntable B 2:1 ratio using a preset detector radius
- b. Turntable A-Turntable B 1:1 ratio using the Turntable B radius preset by a.

c. source - Turntable A 2:1 ratio using the Turntable A radius preset by b. The 2:1 ratios were adjusted in an identical manner but specific reference

Details of spindle sideplay elimination are given in Subsection 3.2.2.g.

will be made to the detector-Turntable B ratio. The detector and turntable were scanned in the reflection configuration through the fine drive range and the position monitor reading was noted at regular angular intervals. The turntable radius arm length was adjusted to minimise drift in the readings. The readings oscillated about a mean over the 5 degree crystal scan range with a pitch of approximately 5 degrees and an amplitude equivalent to a drift in detector position of 12 seconds of arc or 1.3×10^{-3} inch. Similar results to these were obtained for the source-Turntable A ratio.

The 1:1 ratio of the turntables was adjusted by scanning the turntables simultaneously and comparing at a 1 degree intervals the angle generated on one turntable with that of the other turntable. After adjusting the speed ratio the discrepancy between the generated angles was typically 1 second of arc and this discrepancy averaged out over the 5 degree scan range.

3.3.7 Source

The source alignment involved producing an X-ray photograph of the source by a pin-hole camera method as outlined as follows. Slit 1. was set to a small aperture (0.2 mm square) to form the pin-hole and the film was placed in a holder mounted on Turntable A. A beryllium filter was placed behind Slit 1 to block light from the source. A pair of cross-hairs located at the centre of Slit 2 produced an image on the film which referenced the source position about the centre line of the slits. The procedure for taking a photograph involved converting the laboratory to a darkroom, operating the source at typical experimental power settings, inserting the film in a holder through a port in the spectrometer lid and evacuating the vacuum chamber for several minutes. The photograph showed a target area (2.4 mm wide and 7.0 mm high) of uniform emission and the source position was adjusted (see Subsection 3.2.2.d) to set the image of this region symmetrical about the image of the cross-hairs. This adjustment was achieved with an accuracy of approximately 0.1 mm.

3.3.8 Measurement of the detector window transmission ratio

The incident and reflected beam intensities of Crystal B are measured using different windows of the double-sided detector and therefore any measurements which involve ratioing the input and output power of a reflected beam (e.g. peak reflectivity and integrated reflectivity measurements) require correction for differences in transmission between the two windows. The windows at which the incident and reflected beams are monitored are arbitrarily labelled 'External' and 'Internal' respectively on account of their positions with respect to the centre of Turntable B. The internal to external window transmission ratio at a given wavelength was determined by measuring the intensity of a beam monochromated by reflection off Crystal A, firstly with the detector in the I_0 measurement position i.e. immediately behind Slit 3, and then with the detector behind Turntable B crystal mountings with Crystal B removed. The intensity measurement at the I₀ measurement position was then repeated to ensure that there was no change in the beam intensity. The window transmission ratio was simply the ratio of the count rates at the two detector positions and this was used to correct observed I_o values of measurements at the given wavelength. The ratio determination was repeated at other wavelengths to give a plot of transmission versus wavelength for the wavelength range over which crystal characterisation measurements were to be made.

3.4 Operational Procedures

3.4.1 Preliminary procedures

Prior to a comprehensive crystal characterisation the computer programs (see Appendix A) were run for the crystal under study and derived plots showing the wavelength dependence of crystal characteristics were used to guide the experimental programme. The emission line and continuum wavelengths, at which measurements were made, were selected to give a true representation of the wavelength dependence of the measured characteristics over the required wavelength range. It was essential to have prior knowledge of the detector window transmission ratios (see Subsection 3.3.8) for the wavelengths selected because if the ratios were determined after the crystal characterisation there was a risk of invalidating measurements if the fragile detector windows were damaged in between the time of the measurements and the determination of the required ratios. If the crystal to be characterized was susceptible to attack from the laboratory atmosphere then the (1, -1)rocking curve studies were conducted first since the parameters of the (1, -1)rocking curve are senstive to the crystal condition. This was particularly important for measurements on perfect crystals for only in the case of perfect crystals which have suffered no deterioration can the perfect lattice model be tested experimentally.

The first experimental procedure was the preparation of the source which involved inserting a filament and plastic window and coating the target with a cocktail of the materials necessary to generate the required emission lines. If more than say ten emission lines and thus more than one target loading were required the first cocktail contained materials necessary to generate the tilt alignment emission line. In general, tilt alignment is required before any measurements and so the slit apertures were set according to the criteria given in Subsection 2.2.2. These shall be designated as nominal slit settings for in the course of the tilt alignment further adjustment is normally required.

The crystal tilts were then aligned by the X-ray method outlined in Subsection 3.3.3. The alignment was performed at a wavelength for which w_{cc} is small [†](see Subsection 2.2.2) and counting statistics are good. Operation procedures for generating the (1, -1) rocking curves required by the tilt alignment method are given in detail in Subsection 3.4.3. Crystal bending strain, lattice defects and non-uniformity in the crystal surface cause peak broadening which is partially dependent upon the size of the crystal surface reflecting area. The dependence of the profile characteristic w_{cc} upon this area is shown for ADP in Fig.6.8 in which the area is expressed in terms of the size of slit apertures determining the area size. It was possible in the cases of the crystals studied to reduce the nominal slit aperture settings in order to minimise peak broadening and still maintain a sufficiently high beam count rate and $\alpha > w_{cc}$ where α is the horizontal beam divergence (see Section 2.1). Since (1, -1) rocking curve studies contribute a major part to crystal charactisation, details of crystal scan preparations are given in Subsection 3.4.3.

3.4.2 Bragg dispersion function studies

The fundamental measurement required in defining the Bragg dispersion function was the measurement of θ_{λ} (defined in the introduction to Chapter 2) at various reference emission line wavelengths using a single crystal configuration. Each reference line was selected according to the criteria given in Subsection 2.1.a and the source target material chosen to generate that line was either the element of the emission line or a compound containing the element for which the chemical shift of the line was known. The apertures of Slits 1 and 3 could be set sufficiently small to fulfil the resolution

[†] Since w_{cc} decreases with decreasing wavelength the selected wavelength was near the short wavelength end of the o < λ < 2d range.

and vertical divergence conditions given in Subsection 2.1.c. and yet give an acceptable beam count rate. If the angle between the crystal face and the diffraction planes is large or unknown the crystal tilts would have to be aligned by the 2-reflection X-ray alignment method outlined in Subsection 3.3.3. In the case of crystals studied, the tolerance of the manufacture r^{\dagger} on the above angle was about 2 minutes of arc and therefore the crystal could be aligned to within the required tolerance (see Subsection 2.1.c) by setting the tilt micrometer at the nominal optical alignment setting as outlined in Subsection 3.3.3 The crystal temperature was measured by hanging a mercury thermometer inside the spectrometer immediately above the crystal. The thermometer was sealed in a glass tube at atmospheric pressure to ensure that the tank vacuum did not affect the thermometer reading. The supports of this tube insulated the tube from the walls of the spectrometer. The errors incurred in this method of crystal temperature measurement are discussed in Chapter 4.

The procedure for the measurement of θ_{λ} involved scanning the crystal through the peak of the emission line for the crystal configurations A and B shown in Fig.2.1a. The incident beam intensity was measured (see Subsection 3.4.3) before and after each scan merely to ensure that there was no significant intensity change during the course of the scan. Prior to each scan electronic levels were set (see Subsection 3.4.3) and the crystal was scanned rapidly through the peak to determine the final scan range and settings. The latter were selected to give about 30 sampling bins in the peak fwhm and 5,000 counts per bin. In the interest of avoiding excessive scan durations, which introduced errors due to

⁺ Société Quartz et Silice, 8 Rue d'Anjou, 75 - Paris 8. Supplied by Nuclear and Silica Products Ltd., 44-46 The Green, Wooburn Green, High Wycombe, Bucks, HP10 0EU, UK.

^{*} Nevertheless the X-ray alignment method was employed to ensure correct alignment.

changes in source intensity, the scan range was normally little more than the peak fwhm. The chart record was marked and the temperature was recorded at regular angular intervals throughout the course of the scan. The position of each peak was determined from the curve through the mid-points of horizontal chords drawn at different heights through the curve. To fix d₁₈ and α , measurement of θ_{λ} was repeated for a chosen wavelength at different temperatures over a 10^oC range. The crystal temperature was adjusted by altering the temperature controlled laboratory air conditioning. The crystal assumed a new temperature very slowly over a period of several hours due to the thermal inertia of the spectrometer resulting from its large mass. The angle scale was calibrated for each wavelength by the method given in Subsection 3.3.2.

3.4.3 (1, -1) Rocking curve studies

a. General procedure Slit settings for the (1, -1) rocking curve at the tilt alignment wavelength were decided upon by the procedure and criteria outlined in Subsection 3.4.1. At longer wavelengths and hence higher Bragg angles larger horizontal divergence slit apertures may be used for beam reflection off a given surface area. This yields higher beam count rates and also increases α the horizontal beam divergence, which is necessary if $\alpha > w_{cc}$ is to be maintained because for the crystals studied w_{cc} increases with wavelength. For any wavelength at which slit settings were increased (1, -1) rocking curves were obtained for the smaller and larger slit settings to ensure that there was no change in the profile.

The nominal setting of Turntable A for a typical (1, -1) rocking curve was determined by adding the calculated Bragg angle to the zero Bragg angle setting. Turntable A was located at this setting and the source was located at the 20 reflection position using the position monitor as a reference. If,

as is normally the case, emission line radiation is reflected, then Crystal A and the source must be set at the peak position of the line to obtain maximum count rate. The detector was set behind Slit 3 to monitor the beam reflected off Crystal A. Maintaining the phase monitor dip position throughout, the crystal and source were located at other angle settings in several minutes of arc intervals from the nominal setting and were finally located at the setting which gave the maximum count rate.

A proportional counter energy spectrum of the beam reflected off Crystal A was obtained on the multichannel analyser set to accumulative mode. The spectrum is normally made up of contributions from low energy amplifier noise, radiation due to specular reflection if θ is low, the desired emission line radiation, continuum and second order radiation if the source voltage is above twice the excitation potential of the emission line. Normally the source was operated at just below twice the excitation potential but if, for the purpose of obtaining a high count rate, a higher source voltage was required then the detector resolution was normally sufficient to separate first and second order radiation. The amplifier gain and detector voltage were set to give sufficient separation, between wanted X-ray signal and unwanted signal on the pulse height spectrum, to allow discrimination between them. The lower limit of the detector voltage was such that the number of wanted X-ray signal electrons collected was at least three orders of magnitude greater than the number of electrons coming from the counter amplifier system. The upper limit was determined by the limit of proportionality in the detector response. The desired energy band of the spectrum was isolated, such that the counting electronics only monitored radiation in this band, by means of the upper and lower gate levels of the single channel analyser. Each level was set by observing on the multichannel analyser a narrow band pulse from the pulse

generator then adjusting the pulse energy to the upper or lower limit of the required energy band and by observing the ratemeter display adjusting the gate level to the point at which it just discriminates against the pulse. The selected energy band was checked to ensure there was no contamination from low energy noise and second order radiation. The check involved determining the transmission of the beam through a selection of filters and comparing the measured transmission values with those obtained from calculated plots of transmission against wavelength based on literature values of linear absorption coefficients. If the reflected beam was of low intensity the low energy noise could contribute a high proportion to the pulse height spectrum making it impossible to separate this noise from the desired energy band. In such a case a suitable filter was inserted in the beam throughout measurements at that wavelength to discriminate against the low energy noise.

Crystal B was set in the (1, -1) configuration at the nominal angle setting determined as for Crystal A. The detector was located at the 20 reflection position again using the position monitor as a reference. The resultant count rate was usually zero because the (1, -1) rocking curve fwhm is often considerably smaller than the uncertainty in the nominal crystal position and so Crystal B and the detector were scanned (if $w_{cc} \leq 20$ seconds of arc) or pulsed by the coarse drive about the nominal position in order to locate the peak. A pulse height spectrum of the beam reflected off Crystal B was accumulated and the single channel analyser gate levels were set as described above. The source power was then adjusted if necessary to a beam intensity sufficient for good counting statistics (see Subsection 3.4.3.b). The instrument was now prepared for (1, -1) rocking curve measurements.

b. Linear profile study The central region or main body of a (1, -1) rocking curve may be adequately defined by linearly plotting the count rate of the beam reflected off the second crystal against the crystal position. This is easily

achieved by automatically scanning the crystal at a constant angular velocity and monitoring the reflected beam on a linear response chart recorder. A useful preliminary to a linear profile study was a rapid scan through the peak region of the (1, -1) rocking curve to obtain approximate values of P_{cc} and w_{cc} which then guide the choice of scan settings. The linear profile study involved measuring the intensity of the beam incidents upon Crystal B before and after the (1, -1) rocking curve scan in order to check that the intensity did not change by more than a few per cent and to determine the average intensity for the scan which is required for the measurement of P_{cc} . The detector was set behind Slit 3 and by the procedure described in Subsection 3.4.3.a the single channel analyser gate levels were set and the scaler-timer was set to accumulate approximately 10,000 counts. If the incident beam count rate was less than 20c/sec then in the interest of efficiency less counts were accumulated and the background count rate, which for low beam intensities makes a significant contribution to the total count rate, was also determined. The background count rate determination involved offsetting the detector from Slit 3 and, retaining the same electronic settings, accumulating sufficient counts for the uncertainty in the background count rate to be less than $\sim 1\%$ of the true beam count rate.

After measuring the initial incident beam intensity, crystal B was set to the (1, -1) peak position with the detector at the 20 reflection position and the single channel analyser gate levels were set for the scan and background count rate determinations. Crystal B and the detector were then offset from the peak to the side of the peak at which the scan was to be started in order to determine the initial background count rate. The logarithmic wing studies showed that the full range of a (1, -1) rocking curve was normally about sixty times the fwhm and using this criterion Crystal B and the detector were offset well outside this range. The background count rate was determined over a 1000 sec time period. Crystal B and the detector were then set at the scan start position removing coarse and fine drive backlash as described in Subsection 3.3.6. The scan start position was determined by the scan range which was normally about ten times the fwhm. The settings of the peak count rate, the digital ratemeter sample time, the scan speed and the chart recorder were based on the following criteria. An accurate determination of P_{cc} and w_{cc} requires a peak with 25 sampling bins per

fwhm, 2000 counts per bin at the peak, a scan duration of ideally no more than 2 hours (to ensure negligible change in source intensity), a chart record ordinate axis setting giving a peak height of about 10 cms and a chart recorder speed which results in the fwhm corresponding to about 4 cms on the chart record. Typical scan settings were as follows: peak count rate * 200 c/sec sample time = 10 secs; scan duration ≈ 2 hours; chart recorder speed = 200mm/ hr. Immediately before the scan was started the starting angle, sample time, fine drive pulse frequency, chart recorder speed and the correspondence between chart recorder ordinate axis and count rate, were noted. The countertimer was set to zero, the multichannel analyser screen was cleared and using the pulse generator the energy of a pulse was set to the gate level energies in turn using the digital ratemeter to find the energy at which the pulse is discriminated against. The pulse signal was accumulated on the multichannel analyser and in this way the gate levels were marked on the multichannel analyser baseline. This was to ensure that throughout the scan, during which the multichannel analyser accumulated counts, no unwanted radiation was included in the energy band defined by the gate levels and the signal corresponding to the desired radiation did not move out of this energy band due for instance to change in amplifier gain or detector voltage. To start

the scan the Crystal B and detector fine drive micrometers, counter-timer, and multichannel analyser on accumulate mode were set running and the continuously running chart recorder was marked. At the end of the scan the finish angle was noted. Also noted were, the timer reading which by means of a plot of scan speed against fine drive pulse frequency checked that the scan speed was uniform, and the counter reading which gave a rough check on R_{cc} . Crystal B and the detector were offset from the peak and the background count rate determination was repeated. The two positions of Crystal B for the background count rate determinations are symmetrical about the peak. The detector was then set behind Slit 3 and after resetting the gate levels the final beam intensity was measured.

A curve was drawn by hand through the stepped chart recorder trace and from this curve w_{cc} and the peak count rate were measured. The scan background count rate was subtracted from the peak count rate and this was divided by the average incident beam intensity corrected by the detector window transmission ratio (see Subsection 3.3.8) to give P_{cc} .

If the peak count rate is low an inordinate scan duration is required to obtain a peak with counting statistics sufficiently good for an accurate determination of P_{cc} . In this case P_{cc} may be measured separately after the scan as follows. The intensity of the beam incident upon Crystal B was measured and then Crystal B and the detector were positioned at small angular intervals about the peak position using the fine drive micrometer scales to set the intervals and at each position a count rate was accumulated for a time period sufficient for good counting statistics. The peak count rate could easily be determined to an accuracy of $\pm 2\%$ from a hand plot of count rate against Crystal B position. Finally the measurement of the incident beam intensity was repeated and from the average beam intensity and peak

count rate; both corrected as outlined above, P_{cc} was calculated. The method employed for this measurement of P_{cc} is used in the logarithmic profile study and so this measurement could be included as part of that study. c. Logarithmic profile study The wings and peak of a (1, -1) rocking curve differ in height by orders of magnitude and therefore in order to represent both on the same plot the ordinate axis scale must be logarithmic. An automatic scan method using a logarithmic response chart recorder is inadequate because for example in the far wings the count rate is so low that a long sample time would be required to yield good counting statistics and thus to give an adequate number of sample bins in the fwhm an excessive scan duration would be required. In general scan settings would have to be varied for different regions of the peak and this would create practical difficulties. This problem was overcome by stationing Crystal B and the detector at suitable positions in the (1, -1) rocking curve range and at each position determining the count rate over a time period sufficiently long to yield good statistics. In detail the method began by determining the initial incident beam intensity as given in Subsection 3.4.3.b. The detector and Crystal B were then located near the (1, -1) rocking curve peak position and after resetting the electronic levels they were stationed at positions around the centre of the peak and the count rates at these positions were measured in order to determine accurately the peak position (and also the peak count rate from which P_{cc} can be calculated (see Subsection 3.4.3b)). The crystal and detector were stationed at positions increasingly further from the peak until they were outside the (1, -1) rocking curve range at which point only the background count rate was measured. A logarithmic plot of count rate against crystal position was made during the course of the measurements in order to guide the choice of crystal positions such that the minimum number of count

rate measurements were made in defining the (1, -1) rocking curve. In the far wings of the curve counting times of 1000 secs were required and so the incident beam intensity was measured occasionally in order to monitor intensity changes during the long time period required by this experimental method. The incident beam intensity was also measured at the end of the experiment.

The count rate for each crystal position was corrected for the background count rate and divided by the incident beam intensity corrected by the detector window transmission ratio and plotted on a logarithmic scale against crystal position which is defined with respect to the peak position. Typical plots showed the wings extending to 3 or 4 orders of magnitude down on the peak. d. Measurement of the reflection integral and polarisation ratio Two types of measurements using 2-reflection modes were required in the measurement of reflection integrals and polarisation ratios. These were R_{cc} measurements performed in the parallel (1, -1) mode and R_{ab} measurements in the asymmetric reflection mode. The procedure for R_{cc} measurements was essentially identical to the procedure used in the linear profile study, the main differences being that the scan was over the full range of the (1, -1)rocking curve (determined in the logarithmic profile study) and therefore a higher scan speed was used in order to limit the scan duration to a reasonable time period. If the peak count rate was low then the background made a significant contribution to the total count and therefore it was important to use a long counting time in the background count rate measurement to obtain a low uncertainty in the scan background count.

The procedure for R_{ab} measurements involved inserting a large-2d monochromator into Turntable A crystal mounting and then aligning the source and monochromator as described in Subsection 3.4.3.a. The operation procedure was then identical to that of the R_{cc} measurements.
e. Measurement procedures for perfect and non-perfect crystal samples Definitions and processing of perfect and non-perfect samples are given in Chapter 4. In the (1, -1) rocking curve studies of perfect samples, two crystals were removed from their dry-atmosphere sachets and immediately inserted into the crystal mountings of Turntables A and B and the vacuum chamber was immediately evacuated. If, during the course of measurements involving perfect samples, the tank vacuum had to be released, the crystals were immediately transferred to a desiccator. A given crystal sample was always inserted in the same turntable throughout all measurements using that sample, so that small differences between the crystals in surface quality and crystal characteristics did not affect the results.

In all (1, -1) rocking scan studies of non-perfect samples, the perfect sample used in Turntable A for perfect crystal studies was retained as the monochromator and the non-perfect sample was inserted in Turntable B as the test crystal. The reason for this procedure is that the single crystal response of the first crystal can be determined by unfolding the (1, -1)rocking curve of the perfect samples. This means that only the single crystal response function of the non-perfect sample is unknown and this may be determined by unfolding the perfect sample single crystal response function from the measured (1, -1) rocking curve of the non-perfect sample. The present study was restricted to comparing only the (1, -1) rocking curve parameters of perfect and non-perfect samples but for future work a comparison of the parameters of the respective line spread functions is suggested.

3.4.4 Absorption edge studies

In the wavelength region of an absorption edge R_c is normally a rapidly varying, discontinuous function of wavelength. 2-reflection methods for

reflection integral measurements are unsuitable for such a wavelength region because it is impossible to interpolate between reflection integral values measured at different wavelengths and defining $R_c(\lambda)$ by numerous measurements would be inefficient. The problem was overcome by making a single crystal scan through the wavelength region that encompasses the absorption edge. This wavelength region also included wavelengths at either side of the edge at which the reflection integrals had been measured by a 2-reflection method. These measured reflection integral values were used to calibrate the intensity versus wavelength curve obtained from the scan.

The instrument was set up in a single crystal configuration with the crystal inserted in Turntable B and Slits 1 and 3 defining the horizontal divergence of the beam such that the resolution is high enough to resolve the edge and any edge fine structure which may be present. In the wavelength region immediately spanning the edge and at the reflection integral calibration wavelengths a reasonably flat continuum source spectrum was required since the presence of an emission line in these wavelength regions would distort or even mask the characteristic shape of the intensity versus wavelength curve. Any traces on the target of elements which give rise to such emission lines were removed by cleaning the target. This entailed dipping the target for about 10 sec in an etching solution of 6.5 mls distilled water, 1ml HCl (1.16), 30 mls H₂SO₄ (1.83), 12.5 mls HNO₃ (1.40) and then rinsing thoroughly in distilled water.

If the crystal is a chemical compound the absorption edge of the particular constituent element will normally be shifted in energy from the absorption edge of the pure element because of chemical combination. In order to determine the edge shift and also calibrate the angle scale with respect to wavelength the target was lightly coated with compounds which

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produced two reference emission lines. The wavelengths of the reference lines were sufficiently far removed in wavelength from the edge and the reflection integral calibration wavelengths as not to disturb the intensity versus wavelength curve in these regions.

Preliminaries to the crystal scan entailed stationing the crystal at both ends of the scan range in order to select the single channel analyser gate levels necessary to encompass the continuum energy at both ends of the scan. The crystal was then scanned rapidly through the entire scan range in order to decide upon the scaling of the chart recorder ordinate axis and also the sample time and scan speed required to define clearly the edge and any fine structure. The crystal was then scanned using these final settings.

CHAPTER 4

CHARACTERISATION OF PENTAERYTHRITOL (002)

4.1 Introduction

Pentaerythritol (PET, $C(CH_2OH)_4$, $2d \approx 8.74$ Å) is noted for its high reflection efficiency i.e. high reflection integral. Large (- 15 x 8 x 8 cm³) near perfect samples can be economically grown (from water solution) on a commercial scale. PET cleaves easily along the commonly used (002) planes so that precision cutting and optical finishing is not required in sample preparation. The above factors combined with a lattice period of $d \approx 4.37$ Å for the (002) planes, render PET (002) a particularly useful Bragg analyser in the 3 - 8Å soft X-ray region. PET analysers have thus found application in X-ray fluorescence analysis, in the study of laser initiated hightemperature high-density plasmas and was chosen for use in astronomical studies in the ANS spacecraft and in NASA's HEAO-B spacecraft. Clearly PET (002) is sufficiently useful to merit study.

The only notable previous study is that of the author's predecessor Leigh⁸¹ in which PET was one of several crystals studied briefly, as part of a pilot study for a more extensive programme of work. The following study combines and continues the earlier work, to give a detailed characterisation of PET (002) through calculation and measurement.

4.2 Data Sources and Details of Numerical Evaluation

The atomic co-ordinates and unit cell parameters were obtained 102 from Wyckoff (Vol. 5, p.7). At the time of executing the PET calculations allowance for temperature effects was made by the Debye-Waller method only (see Sec. 1.7). It is uncertain what value should be chosen for the Debye temperature factor M but not significant effect on results was found for any value in the range of 0 < M < 0.1which are reasonable limits to M so, M was set to zero. A later inclusion in the calculations allowing for isotropic and anisotropic temperature parameters prompted a search for such parameters. Since only crude isotropic temperature parameters¹⁰⁴ were available it was finally decided that there should be no inclusion of temperature effects in the PET calculations. The crystal density (1.39 grms/cc) 105 was given in the manufacturer's data sheet.

Atomic scattering factors required for all crystals studied were calculated from analytical expressions based on calculations using Hartree-Fock wavefunctions (see Sec. 1.3 and Appendix A).

Since the constituent atoms of PET are low Z elements and the photon energies relevant to Bragg scattering are considerably higher than the absorption edge energies of these atoms, the approximations employed in deriving Expressions (1.21k).(1.21k) can be made. Also the K electrons of the constituent atoms of PET can be approximated as hydrogenic wavefunctions and thus Honl's calculation is appropriate to the calculation of the anomalous dispersion terms of atomic scattering factors. Expressions (1.21n), (1.21o) were evaluated for all K-shell orbitals in PET. It is clear from Expression (1.24) that once $\Delta f''_{i}(\omega)$ is found for a given atom, then the linear absorption coefficient is easily found. This was done and the results compared favourably with the measured data of Stainer's catalogue thus generating confidence in the employed Horl calculations. Linear absorption coefficients were calculated from anomalous dispersion terms, for PET and all other crystal calculations.

4.3 Bragg Dispersion Function Measurements

Measurements of the Bragg dispersion function were made using a good quality UK5 crystal sample. The emission line Ca Ka₁ was chosen for measurement of d₁₈ and a since at this wavelength the contribution to θ_{λ} from anomalous dispersion is 0.2" and therefore can be neglected. The Ca Ka₁ line was generated using CaO and hence the wavelength of the line was corrected for chemical shift. Numerical details of the shift and corrected wavelength are given in Table 1. The uncertainty on the wavelength arising from uncertainty on the chemical shift could only be estimated on the basis that chemical shift values are quoted to 0.01 év and therefore any error in the chemical shift must be a small integral number times this value. Although only one value for the chemical shift could be traced, for other lines for which there are more than one measured value, the values vary by about 0.02 ev and this was adopted as the uncertainty on the chemical shift of the Ca Ka₁ line.

Measurements of θ_{λ} were made over the temperature range 18 - 25°C. Details of the measurements together with the corrections to θ_{λ} (meas.) are given in Table 1. The uncertainty on θ_{λ} measurements (excluding uncertainties due to temperature variations) is 2.2".

A calculated value for $\Delta\theta$ of 13.5" was subtracted from each θ_{λ} value to give θ_{B} values. A plot of d (derived from θ_{B}) against temperature T is shown in Fig. 4.1. The best line through the points, obtained from a weighted linear regression of T upon d, gives values for d_{18} and α as below. Literature values are also shown.

	d ₁₈ (Å)	α (x 10 ⁴)
This work	4.3679±0.0003	1.1±0,1
Literature values	4.363±0.001	1.2±0.08'06
	4.37±0.01 ^{'°4}	

Clearly there is good agreement between the measured values of this work and literature values. It should be noted that the centroid of the data points in Fig. 4.1 is close to 23° C rather than to 18° C. Since the standard error on points along the best line is a minimum at the centroid it is preferable for the centroid of the data points to be close to the standard crystallographic temperature 18° C. This could not be achieved due to the difficulty of maintaining the instrument temperature lower than about 17° C. The more accurate value for d obtained at 23° C is $d_{23} = 4.3703\pm0.0001 \text{Å}$. In spite of the above difficulty the uncertainty on d_{18} is considerably smaller than the uncertainties of previous measurements.

The determination of $\Delta \theta$ (λ) for PET required measurement of $\Delta \theta$ at wavelengths near the middle and the long wavelength end of the PET wavelength range. The emission line Cl K α_1 was selected for measuring $\Delta \theta$ near the middle of the wavelength range. This line was selected on account of the fact Bearden's wavelength tables gives the wavelength for NaCl and since this was used as the target material in this work there is no need to correct for chemical shift. However, this emission line is omitted from Table 2.1 which lists reference wavelength lines for this wavelength region. This table was compiled after the present work and on reflection if this table had been available at the time of this work then Cl $K\alpha_1$ would not have been chosen. Nevertheless Bearden's error estimate for C1 K α_1 wavelength is 21 ppm (see Table 4.2) which is adequately small for the present work. The emission line Si Ka, was selected for measuring $\Delta \theta$ at a long wavelength. The line was generated using SiC for which the chemical shift is known. Numerical details of the shift and corrected wavelengths are given in Table 4.3. The uncertainties on θ_{λ} measurements for C1 Ka₁ and Si Ka $_{1}\,$ are 2.3" and 2.76" respectively. These uncertainties exclude

uncertainties due to temperature variations. $\Delta \theta$ was evaluated, by the method outlined in Section 2.1, for Cl Ka₁ and Si Ka₁ using the results shown in Tables 4.2 and 4.3 respectively together with α and d₁₈ determined from the Ca Ka₁ data. The measured and calculated results are as follows

Line	λ (Å)	Δθ (calc.) (arc sec)	Δθ (meas.) (arc sec)
Cl Ka ₁	4.7278	21.2	13.9±5.6
Si Ka _l	7.12453	46.9	45.2±9.5

The two measured values are shown on a plot of calculated $\Delta \theta$ (λ) in Fig. 4.2.[†]

A comparison of measured and calculated values of $\Delta \theta$ shows that the measured $\Delta\theta$ values reveal the general trend of $\Delta\theta$ (λ) but the uncertainties on the measured values are too large to allow a clear definition of $\Delta \theta$ (λ). The magnitude of the uncertainties is due mainly to the large uncertainty on θ_1 arising from temperature variations which in turn arise from the large α of PET. Uncertainties arising from this source are approximately 5 times greater than those arising from other sources discussed in Subsection 2.1.c. Furthermore the method employed for temperature measurement incurs uncertainties which are difficult to estimate. For instance the thermometer measures the temperature inside the vacuum chamber but does not measure the crystal temperature directly. If the determination of $\Delta \theta$ (λ) is to be part of future measurement programmes then crystal temperature control and measurement must be significantly improved. In summary, the large α of PET allows accurate measurement of α itself but gives rise large uncertainties on $\ \Delta \theta$ () .

Note that, for the analysers studied (with the exception of ADP), the contribution to $\Delta\theta$ from anomalous dispersion is too small to allow graphical distinction between $\Delta\theta$ and the contribution to $\Delta\theta$ from normal dispersion alone.

Line	Ca Ka
Target material	CaO ¹
Chemical shift	-0.41ev *
λ (corrected)	3.35876±0.00004Å

Corrections to $\theta_{\lambda}(\text{meas.})$

$\Delta\theta$ (ang.)	8.2"
Δθ (ψ)	-0.4"
∆θ(abs.)	0.2"

Tempe (Scan 1	orature OC) Scan 2	Mean Temp. (^O C)	$\theta_{\chi}(meas.)$	θλ
17.3	18.9	18.1	22 ⁰ 36' 46''	22 ⁰ 36' 54''
20.0	21.0	20.5	22 ⁰ 36' 25''	22 ⁰ 36' 33''
20.2	21.4	20.8	22 ⁰ 36' 21''	22 ⁰ 36' 29''
21.3	22.5	21.9	22 ⁰ 36' 10''	22 ⁰ 36' 18''
22.2	23.0	22.6	22 ⁰ 36' 06''	22 ⁰ 36' 14''
23.0	24.2	23.6	22 ⁰ 35' 52''	22 ⁰ 36' 00"
23.3	24.9	24.1	22 ⁰ 35' 51.5"	22 ⁰ 35' 59.5"
23.6	25.0	24.3	22 ⁰ 35' 50''	22 ⁰ 35' 58''
24.3	24.8	24.55	22 ⁰ 35' 46.5''	22 ⁰ 35' 54.5"

Table 4.1 PET (002) Bragg dispersion function Measured data for Ca $K\alpha_1$

LineC1 K α_1 Target materialNaC1Chemical shiftNo correction, required (see text) λ 4.7278±0.0001Å

Corrections to $\theta_{\lambda}(\text{meas.})$

∆θ(ang.)	6.3"
Δθ(ψ)	-0.6"
$\Delta \theta$ (abs.)	0.4"

Temperature (^O C)		Mean Temp.	$\theta_{\lambda}(meas.)$	θλ	
Scan 1	Scan 2	(⁰ C)	1		
17.5	19.8	18.65	32 [°] 46' 20''	32 [°] 46' 26''	
24.2	25.1	22.83	32 [°] 44' 49''	32 [°] 44' 33''	

.

Table 4.2 PET(002) Bragg dispersion function Measured data for C1 K α_1

Line	Si Ka,
Target material	SiC
Chemical shift	0.22 ev +
λ (corrected)	7.12453±0.00013Ä

Corrections to $\theta_{\lambda}(meas.)$

$\Delta\theta$ (ang.)	3.3"
Δθ(ψ)	-1.2"
$\Delta \theta$ (abs.)	1.7"

Temperature (°C)		Mean Temp. θ_{λ} (meas.)		θλ	
Scan 1	Scan 2	(°C)			
17.1	18.7	17.9	54 ⁰ 39' 32''	54 ⁰ 39' 36''	
23.0	23.8	23.4	54 ⁰ 36' 53''	54 ⁰ 36' 57"	
22.9	24.1	23.5	54 ⁰ 36' 12''	54 ⁰ 36' 16"	
25.8	26.7	26.3	54 ⁰ 34' 33''	54 ⁰ 34' 37''	
25.7	27.1	26.4	54 ⁰ 34' 12"	54 ⁰ 34' 16''	

Table 4.3 PET(002) Bragg dispersion function Measured data for Si $K\alpha_1$





PET(002) Lattice period versus temperature plot for Ca Kal measurements. The plot shows the measured data points and the best line obtained from a weighted linear regression of T upon d .



Figure 4.2 PET(002) The shift of $P_{\lambda}(\theta)$ from the simple Bragg angle θ_{B}

4.4 Line Spread Function Measurements

4.4.1 The Bragg reflection integral

a. Comment on the calculated results

Two (related) matters are immediately clear from inspection of Fig. 4.3. The Darwin zero-absorption result is everywhere quite close to the Prins result, even near the long wavelength limit. This can be interpreted as being due to the unit cell absorption cross section being everywhere much smaller than the corresponding scattering cross section. This factor also causes the Darwin zero-extinction function to be everywhere much larger than the Prins result. This latter is interesting. Figure 4.3 shows that in any spectrometer whose total light throughput is proportional to R_c^n , [†] a sample of PET (002) which is described by the zeroextinction function is more 'efficient' than a perfect sample by about factor 4 at 7Å and by more than factor 10^2 at 1Å. Although the primary interest of this work is in first order diffraction it is useful to have information on higher order results for the sake of users making higher order measurements and also in order to estimate where necessary the magnitude of higher order contamination in first order experimental studies. The calculated results for orders n = 1-4 are shown in Fig. 4.7. The higher order results are over an order of magnitude down on the first order result and therefore it can normally be expected that higher order contamination of reflected first order radiation will be small.

b. Measurements

Nearly all measurements of the Bragg reflection integral R_{c} were made using the dispersive asymmetric 2-reflection configuration

⁺ Superscript n refers to the reflection order. Wherever this superscript is omitted, first order reflection should be assumed.

with potassium acid phthalate as the monochromator. The R_c values for aged material were derived from R_{cc} values of the (1,-1) parallel configuration. R_c was also derived from R_{cc} measurements for perfect material at long and short wavelengths 8.34 and 2.75Å since at these wavelengths the uncertainty in the polarisation correction required to evaluate R_c from R_{cc} is small thus little extra advantage is gained from the asymmetric configuration method. The results presented have been corrected for polarisation bias incurred in 2-reflection measurement methods.

<u>i. Perfect material</u> Several samples of solution grown PET, cleaved to expose the 002 planes, were obtained.⁺ They were handled, shipped and stored prior to use with some care and in sealed desiccated containers. Results of R_c and R_{cc} measurements are shown by filled circles in Figs. 4.3, 4.4 respectively. The general key to the graphs is given on the page preceding them. Measurement uncertainties on R_c values of all materials are in general 6% or less and on R_{cc} values, 2% or less. Fuller details of measurement uncertainties are given in Tables 4.4, 4.5.[‡] The measured values are everywhere satisfying close to the predictions of the Prins model so that from this (restricted) point of view the material may be regarded, even in its surface layers, as possessed of nearly perfect lattice structure. This latter conclusion must be tested against the results of other crystal characteristic measurements.

<u>ii. Aged material</u>. Following the above study the samples were in intermittent use in general laboratory conditions for a period of

^T Manufactured by: Quartz et Silice, 8 rue D'Anjou, 7508 Paris. Supplied by: Nuclear and Silica Products Ltd., 44-46 The Green, Wooburn Green, High Wycombe, Bucks. HP10 OEU, U.K.

⁺ In general measurement uncertainties are included in the result tabulations rather than in the figures (as error bars) in order to avoid confusing the figures.

about two years, and the measurements were repeated; measured results for the sample used two years previously for the fresh stock study are presented (open circles) in Fig. 4.3, 4.4. The R_c results were derived from R_{cc} values hence the measurement uncertainties on R_c at 4.85Å and 7.13Å are appreciably greater than at other wavelengths (see Table 4.4) on account of the larger uncertainties on the polarisation corrections, a full explanation for which is given in Section 2.2.1. A dramatic change in the properties of the sample is clearly seen and this is attributed to chemical attack on the material by the laboratory atmosphere. It can be expected that any such chemical action will disturb the lattice in such a way as to reduce both the primary and secondary extinction coefficients and thus change the function R_c^n (λ) in the direction of the zero-extinction limit.

<u>iii. Sample spread of characteristics</u>. It follows from the above description of the marked aging instability of the characteristic of the given sample that one must expect substantial spread of the characteristics of a given selection of samples according to their individual histories. However, based on tests of three samples, it has been found that the quality of analysers supplied by Nuclear and Silica Products Ltd. is such that analysers, when freshly supplied, are closely described, say to within a few percent, by the typical result shown in Fig. 4.3.

iv. Processed material. The large factor which separates the zero-extinction and perfect lattice functions for $R_c(\lambda)$ suggest that, at the expense of crystal resolving power, it is possible to increase the reflection integral by damaging the crystal surface thereby reducing extinction. The manufacturer supplied samples of

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PET which had been subjected to a proprietary process in order to induce such surface damage. This process was solution etching using water as the solvent. Measured results for R_c and R_{cc} for one such treated sample are shown as open triangles in Figs. 4.3, 4.4. This shows that substantial improvement in the efficiency of the material is indeed achieved compared with that of the perfect material. However, this function is still a long way short of the theoretical limit.

It was thought that perhaps a 'less gentle' damage process might produce further improvement. Samples of PET (002) were subjected to a number of more or less violent damage processes which included rapid recrystallisation of the surface from water solution, steam blasting, and grit blasting using $50\mu Al_0$ grit. Most such processes could be controlled to produce a uniform matt surface but X-ray testing showed erratic ill-formed Bragg peaks (see Subsection 4.4.2). One such process, though, always gave reproducible Gaussian-like shapes. This process was a gentle hand polishing with a No. 220 silicon carbide grit. This treatment also resulted in a uniform matt surface. The measured results for R_{c} and R_{cc} for the SiC abraded samples are represented by filled squares in Figs. 4.3, 4.4 respectively. These show that, for example, at 3.36Å the net improvement over the value for the perfect sample is about factor 6 with only about factor 2 remaining to reach the theoretical limit.

c. The polarisation ratio

In order to use a Bragg analyser for the measurement of polarised beams, or to determine such polarisation by use as polarimeter, a separate knowledge of the two functions $R^{n}_{C\pi}(\lambda)$, $R^{n}_{C\sigma}(\lambda)$ is required. Since $R^{n}_{C}(\lambda)$ is available as above then

from Eqns. 2.41, 2.42, it is seen that the additional knowledge of the polarisation ratio $k^{n}(\lambda)$ allows calculation of $R_{c\pi}^{n}(\lambda)$, $R^{n}_{c\sigma}$ (λ). At chosen wavelengths R_{cc} and R_{c} were measured by the (1, - 1) parallel method and (1, - 1) asymmetric configuration method respectively and k was determined from the quotient R_{cc}/R_{c} using Eqn. (2.44). Measured values of R_{cc}/R_{c} and k, as a function with $\theta_{\rm R}$, are shown as filled circles on Figs. 4.5, 4.6 respectively. Measurement uncertainties on R_{cc}/R_{c} are ~ 6% or less. Upper and lower limits on k values are given in Table 4.6. Also shown are the result derived from the Prins perfect lattice calculations and the trivial solutions $k(\theta_B) = |\cos 2\theta_B|$, $\cos^2 \, 2\theta_{_{I\!\!R}}$ which respectively arise at the Darwin zero-absorption and zero-extinction limits. The measured values of the perfect material are close to the perfect lattice limit for $\theta < 45^{\circ}$ whereas for θ > 45 $^{\rm O}$ the measured values tend towards the zero-extinction limit. A possible interpretation of this behaviour is that the bulk of the crystal material is indeed well described by the Prins calculation but that the topmost surface layers are much less perfect and better described by the zero-extinction limit. It can be expected that measurements at longer wavelengths with smaller extinction depths, and higher absorption, will be more sensitive to surface damage than short wavelength measurements. However, the trend in the measured k (θ_{R}) result does not appear to be in accordance with the measured R_c (λ) result nor with the measured w_c(λ),w_{cc}(λ) results, both of which indicate that the sample is close to the perfect lattice limit at all wavelengths. The $w_{c}(\lambda)$, $w_{cc}(\lambda)$ results in Figs. 4.8, 4.9 respectively show that if the material is mosaic then the mosaic spread must be very small. The difference in the trends of the $k(\theta_B)$ and $R_{c}(\lambda)$, $w_{c}(\lambda)$, $w_{cc}(\lambda)$ results prompts the following comments.

The uncertainties on the $k(\theta_B)$ result are much higher than on the other results so that a strong **case** explaining the difference cannot be built upon the basis of the former result. It is also possible that at long wavelengths $k(\theta_B)$ is much more sensitive to mosaic characters than the other results. In the case of $R_c(\lambda)$, for example, Fig. 4.3 shows that the difference between the Prins perfect lattice and zero-extinction limits decreases with increasing wavelength so that at longer wavelengths (where for reasons discussed above mosaicity ought to be more significant) $R_c(\lambda)$ is less sensitive to crystal mosaicity. Figure 4.6 shows that for k, differences between the Prins and zero-extinction limits are of comparable magnitude at short and long wavelengths so that sensitivity towards mosaicity is also comparable.

The measured values for the manufacturer's processed material are shown as open triangles in Figs. 4.5, 4.6. At small angles the values lie between the perfect lattice and zero-extinction limits. This is to be expected on the basis of the $R_c(\lambda)$ result of the processed material. At high angles following a trend similar to that exhibited by the perfect material the R_{cc}/R_c and k values have gone to the mosaic limit. These results indicate that the damaged layer has thickness comparable to the $7A^\circ$ (θ =55°) penetration depth but is not so thick as the $3A^\circ$ (θ =20°) penetration depth. Measured values for the SiC abraded sample (represented by filled squares in Figs. 4.5, 4.6) show that for $\theta>32^\circ$ or so (and thus for $\lambda>4.4A$) the sample is quite closely described by the zero-extinction limit. At $\theta \sim 30^\circ$ ($\lambda \sim 4.3A^\circ$) there is a transition towards behaviour close to the Prins prediction as the wavelength apparently becomes short enough to penetrate the surface damage. It is interesting to note that there are reports in the literature of values of k lying outside the Darwin limits of $^{84},108$ $|\cos 2\theta|$ and $\cos^2 2\theta$. On occasion this has been observed in this laboratory but the cause has been due to an experimental procedure mistake, for instance not allowing sufficient scan range to encompass the extensive wings of a mosaic crystal rocking curve. A repeat run after removal of the mistake has always yielded an interpretable result. Figure 4.6 shows that the long wavelength point of the SiC abraded sample is below the $\cos^2 2\theta$ limit. This point was calculated from data runs made for the purpose of R_{cc} , R_{c} determinations only and has much larger uncertainty (shown by its error bar) than would normally be accepted. Allowing for the large uncertainty, the point plotted is not inconsistent with Darwin theory.

d. Discussion

The satisfactory agreement between the calculated and measured $R_c(\lambda)$ and $R_{cc}(\lambda)$ results for the case of the perfect material is an important indicator of the freedom from error in the methods of both calculation and measurement. The indication from R_{cc}/R_c and k measurements, of some mosaic character in the surface layers is to be expected on account of the softness and high water solubility of PET. With the calculation of the perfect case supported by direct measurement in this way, there is little chance that the calculated zero-extinction limit can be much in error, even though no material could be found to closely approximate to that limit. It is noted that the very large calculated ratio of the zero-extinction to perfect lattice limit $R_c(\lambda)$ values can be expected to cause vulnerability in the stability of the characteristic of given sample against given surface damage. Recognising again that PET is in fact highly water soluble, a fairly substantial age changing of the characteristic of an initially near-perfect sample can be expected. Such changes were in fact measured. It follows that one can expect substantial spread in the $R_c(\lambda)$ characteristics of different analysers according to their individual histories. The process of producing a mosaic crystal sample might be thought of as little more than accelerating the change that occurs anyway on exposure of PET to the atmosphere. It should be noted that increase of spectrometer efficiency in this way is achieved, as shown and discussed in Section 4.4.2 below, at the expense of loss of resolution due to broadening of $P_{\lambda}(\theta)$.

Line	λ 0 (A)	Perfe Direct	ct Fit	Aged [†]	Proce S,QαS	essed SiC grit polished
Ti Kα	2.75	5.3+	5.52	21.7		
Ca Ka	3.36			19.1	17.6	39.9
Κ Κα	3.74	7.2		15.2		
Ru La	4.85	8.1	7.46	12.7±9%	15.4	23.0
Nb La	5.73	8.1	7.92	12.2		
Ρ Κα	6.16	8.6	8.28			
Si Ka	7.13	13.2	13.4	16.7±8%	17.2	16.6
Continuum	7.9	22.9	23.2			
Al Ka	8.34	45.1 +				
		±6%		±5%	±5%	±6%

Table 4.4 PET (002) Measured values of the Bragg reflection integral R_c (rads x 10⁵) [†] Result derived from R_{cc} measurement. All other results are derived crom R_{ab} measurements.

	λ	Perfect			Processed		
Line	(A)	Direct	Fit	Aged	S,QαS	SiC grit polished	
Ti Kα	2.75	5.6	5.60	22.8			
Ca Kα	3.36			21.3	18.8±4%	42.8	
Κ Κα	3.74	7.0		17.8			
Ru La	4.85	9.75	9.73	19.9	21.3	36.0	
ND LA	5.73	14.3	14.2	23.7			
Р Ка	6.16	17.0	16.6				
Si Kα	7.13	19.6	19.3	27.3	28.6	30.4±4%	
Continuum	7.9	26.0	25.6				
Al Ka	8.34	46.9					
		±1%		±1%	±2%	±1%	
Table 4.5	Table 4 5 PFT (002) Measured values of the 2-reflection						

Table 4.5 PET (002) Measured values of the 2-reflection integral R_{cc} (rads x 10⁵)

λ	θ	Perfect		Processed SiC grit	
(A)	(degrees)	Direct	Fit	S,QαS	polished
2.75	18.37		0.783		
3.36	22.65			0.59 (.86) (.47)	0.58 (.66) (.47)
3.74	25.38				
4.85	33.77	0.38 (.42) (.34)	0.289	0.24 (.27) (.21)	0.14 (.17) (.12)
5.73	41.05	0.07 (.10) (.04)	0.056		
6.16	44.91	0.006 ^(.02) (.000)	0.000		
7.13	54.80	0.18 (.22) (.15)	0.203	0.10 (.14) (.07)	0.05 (.09) (.01)
7.9	64.87	0.46 (.49) (.44)	0.517		

Table 4.6 PET (002) Measured values of the polarisation factor $\,k\,$ Upper and lower limits are given in brackets.

Key to summary graphs

	Darwin zero-absorption limit
	Darwin zero-extinction limit
	Prins perfect lattice limit
•	Perfect material
0	Aged material
· · · · · · · · · · · · · · · · · · ·	Processed material - manufacturer's treatment
•••••	Processed material - SiC grit polished.



Figure 4.3 PET(002) Bragg reflection integral



Figure 4.4 PET(002) 2-reflection integral







Figure 4.7 PET(002) Bragg reflection integral for reflection orders n = 1 - 4

4.4.2 The function

a. Measurements

i. Perfect material. Two fresh samples of PET were used to generate a series of (1, - 1) rocking curves. Values of $w_{\rm cc}$, $\left(\Delta\lambda/\lambda\right)_{\rm cc}$, P_{cc} for these rocking curves are presented in Figs. 4.9, 4.11, 4.13. Measurement uncertainties for all materials except SiC grit polished samples are typically 3% on w $_{\rm cc}$, $\left(\Delta\lambda/\lambda\right)_{\rm cc}$ and 2% on P $_{\rm cc}$. Fuller details are given in Tables 4.7, 4.8. For $\lambda > 5 \stackrel{o}{A}$ there is a good agreement between the measured and the calculated perfect lattice result. For short wavelengths and hence low glancing angles there is a large difference between the calculated and measured result. This is due to the measurements being made under broad beam conditions, i.e. the beam width at Crystal B is > 2mm . At the low glancing angles of short wavelengths large areas of crystal surface are irradiated and therefore 'ripple' in the lattice planes, arising from bending strain and imperfect crystal growth, becomes significant. Also since the line spread function is narrow at short wavelengths, lattice defects will, in terms of distortion of the function, have a proportionately greater effect at short wavelengths than at long wavelengths. The distortion of (1, -1) rocking curves at low glancing angles (at short wavelengths) is treated more fully in Chapter 5. Taking the effect of the broad beam condition into account and the possibility of crystal mosaicity as discussed in Subsection 4.4.1, Fig. 4.9 shows that if the crystals are mosaic to any degree then the mosaic spread must be very small.

In view of the fact that at all but the shortest wavelength measurements, the agreement between calculated and measured results is good, an attempt was made to fit the self-convolution of perfect lattice function to the measured (1, -1) rocking curves. A fit to within a few percent of the peak and fwhm of each rocking

curve was obtained. Details of the fit parameters are given in Table 4.9 and in Figs. 4.16, 4.17, 4.18. An outstanding feature of these results is that at 2.75\AA , where the difference between measured and calculated results is large, the fit parameters are strikingly different from the parameters at other wavelengths. This is because at $2.75\overline{A}$ a large perturbation of the perfect lattice function was required in order to obtain a fit. At other wavelengths the fit parameters are such as would be expected for a small perturbation of the perfect lattice function, i.e. the fwhm of the major Gaussian spread function is narrow with respect to the perfect lattice function, and the minor Gaussian spread function makes a very small contribution to the total spreading of the perfect lattice function. The fit to the (1, -1)rocking curve is presented superimposed on the rocking curve for each wavelength in Figs. 4.19.1a,4.24.1a. The self-convolved perfect lattice fit function is shown by the continuous line and the (1, - 1) rocking curve by the dotted line. These figures show that apart from at 7.9\AA the fit is good to all regions of the rocking curves.

The parameters w_c , $(\Delta\lambda/\lambda)_c$, P_c of the perfect lattice fit function are shown as filled circles in Figs. 4.8, 4.10, 4.12. For $\lambda > 5 Å$ the fit result still closely follows the trend of the perfect lattice result which is to be expected since the required perturbation to the perfect lattice function in this wavelength region is small. It is also worth noting that the difference between the fit and perfect lattice result is close to the difference between the measured result and the 2-reflection perfect lattice result. Intuitively this is a reasonable outcome. The fit functions obtained in the wavelength range were thus regarded as acceptable approximations to the perfect material line spread function. The results for the fit function at 2.75\AA° are far removed from the perfect lattice function. In view of the gross perturbation of the perfect lattice function required to obtain a fit at this wavelength this fit function was regarded as an unacceptable description of the perfect material line spread function.

Plots of the fit and Prins perfect lattice functions for σ -, π - polarised and unpolarised radiation are presented in Figs. 4.19 - 4.24. In all cases the curve with lower peak reflection and higher wings is the fit function. It is noticeable that the shape of the fit function is closer, at long wavelengths, to the perfect lattice function than at short wavelengths. This is due to the fact that only a small degree of perturbation of the perfect lattice function was required at the longer wavelengths. For example, at 4.85Å a 30% adjustment of the width of the 2-crystal perfect lattice function was required whereas at 7.13Å this adjustment was only 10%. It is useful with regard to the point made to compare Figs. 4.19 - 4.24 with Figs. 6.19 - 6.27 for ADP (101) the measured result for this crystal being close to the calculated result at all wavelengths.

<u>ii. Aged material</u> A description of the aged material is given in Subsection 4.4.2 above. Measured results for w_{cc} , $(\Delta\lambda/\lambda)_{cc}$ are shown as open circles in Figs. 4.9, 4.11 respectively. w_{cc} for this material shows an increase over the perfect material by about factor 5 at all wavelengths. This increase can be attributed to the fact that chemical attack by the laboratory atmosphere gives rise to mosaic character in the crystal. In terms of the simple domain structure model the broad domain orientation distribution caused by chemical attack increases the line spread function fwhm and

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consequently w_{cc} . Since there is no limiting value for the fwhm and peak of the 2-reflection zero-extinction function one cannot judge where the measured results lie with respect to the zeroextinction and perfect lattice limits. Only a comparison with other samples of varying degrees of crystal perfection is possible.

<u>iii. Sample spread of characteristics</u>. The above results show, as was found for the Bragg reflection integral, a large change of characteristics between perfect and aged samples and therefore a considerable spread of characteristics is to be expected for samples which have undergone varying degrees of aging and treatment. Again there was only a small spread of characteristics for the freshly supplied near-perfect samples.

iv. Processed material. It is clear from the aged sample results that the increase in the Bragg reflection integral, above the perfect sample value, is at the expense of loss of resolution. This is also found for the manufacturer's surface treated samples, results for which are shown as open triangles in Figs. 4.9, 4.11, 4.13. Wcc is up by factor 4 on the perfect sample result and P_{cc} is down by about factor 2.5 for $\lambda > 5A$ but towards shorter wavelengths the difference in P_{cc} between the perfect and processed sample result decreases rapidly. The latter suggests that distortion of the (1, - 1) rocking curve at small glancing angles (see paragraph i. above) is not as predominant as it is for perfect samples. Note that the processed sample w_{cc} , P_{cc} results follow the trend of the perfect lattice result even at low angles. This is to be expected for since the 2-reflection line spread function fwhm is large so the effect of those defects accentuated at low glancing angles will be less significant. This of course assumes that some of the defects at least do not increase in proportion to the fwhm increase. One

such defect for example is that arising from bending strain.

In the attempt to increase reflection efficiency, by subjecting samples to various surface treatments (outlined in Subsection 4.4.1), it was important to find a treatment which did not incur severe loss of resolution or, distortion of the line spread function. The treatments to which samples were subjected are outlined in Subsection 4.4.1 and the measured characteristics are presented in Table 4.10 for Si Ka and Nb La . The rocking curve for the steam blasted sample shows a relatively small increase in w above the untreated sample but as mentioned previously this technique was rejected since it produced no increase in the reflection efficiency. The characteristics of the sand blasted and SiC polished samples are similar; w_{cc} for these treated samples is up by factor 7 on the untreated sample. The grit blasting technique was rejected because, as seen in Fig. 4.25b, the rocking curve has high wings with only a small fraction of the counts in the main body of the peak. The rocking curve of the SiC polished sample, shown in Fig. 4.25 d has a Gaussian - like shape with most of the counts in the main body of the peak. The rocking curve of other samples polished with SiC were similar with respect to shape and parameters thus showing therepeatability of the technique. The sand blasting technique on the other hand gave non-reproducible rocking curves. The SiC polishing treatment was thus chosen as the techniques used to increase sample reflection efficiency. The (1, - 1) rocking curve parameters for a pair of SiC polished samples are shown as filled squares in Figs. 4.9, 4.11, 4.13. The low $P_{cc}(\lambda)$ characteristic of the SiC grit polished samples gives rise to low count rates, hence on account of poorer counting statistics the measurement uncertainties on

 w_{cc} , $(\Delta\lambda/\lambda)_{cc}$ and P_{cc} values are higher than for other materials (see Tables 4.7, 4.8). The most notable feature of the results is the high wavelength dependency of the parameters. This is also seen in the Bragg reflection integral result. The result shows no sign of rocking curve distortion at small θ , an explanation for which is given above.

b. Discussion

Agreement between the measured and calculated result for perfect material is good except, for reasons summarised below, at short wavelengths. This confirms, as for the $R_c(\lambda)$ result, the validity of the calculations and measurements.

At all but the shortest wavelength implementation of the procedures discussed in Subsection 2.2.2.d successfully produced model (1, - 1) functions which closely matched the measured functions; the model line spread functions generated by this process were indeed only small perturbations from their parent Prins calculations. Consequently there is a good confidence, from the arguments of Subsection 2.2.2.d that these modelled line spread functions are rather good estimates of the behaviour of the analyser.

At the very shortest wavelength λ 2.75 implementation of the same procedures appears to be equally successful in producing a model fit to the data but the perturbations required to the parent Prins function were uniquely in this case proportionately much larger hence there is correspondingly lower confidence that the model line spread function is a unique representation of the behaviour of the analyser. The reason for the difficulty found at this short wavelength (and for the related discrepancy between the measured and calculated result referred to above) became apparent in a subsequent investigation (see Subsection 5.4.2) when it became clear that an additional factor was involved. Specifically, at small glancing angles fixed aperture measurements refer to very much larger working areas of the crystal and the chance of a macroscopic lattice deformation occurring in that used area quickly increases. This kind of defect is not explicitly modelled in the fit procedures. The apparent success in obtaining a fit is therefore due to fortuitous adjustment of those free parameters in the program originally included to model other processes. The net result of all this can be summarised in the statement that there is lower confidence than usual that the result reported at $\lambda 2.75$ is uniquely correct.

Throughout all measurements a correspondence between increase in R (λ) and loss in resolution was found. This is to be expected since for any reduction in the extinction limitation on R_c there is a commensurate increase in the width of the orientation distribution of the crystal domains. The (1, - 1) rocking curve width is some 3 arc minutes for a sample which has received the manufacturer's proprietary surface treatment and is some 20 arc minutes for the SiC grit polish method. Note that line peak count rate actually diminishes once the width of $P_{\lambda}(\theta)$ is taken above the angular width of the beam collimation used, even though the value of R_c may be further increasing. That is to say that, in such a case, the beam collimation in use must be widened, so as to be kept larger than the width of $P_{\lambda}(\theta)$, for advantage to be taken of the increased beam throughput capability of the analyser. In materials analysis machines, for instance, where beam collimation to 6 arc minutes is used, the manufacturer's surface treatment process discussed above is about optimum for most efficient operation. In cases where the loss of resolution that accompanies change of collimation to 30 arc minutes can be tolerated (e.g. in the detection of line radiation from X-ray stars) a further substantial improvement is available by the grit abrasion method.

Line	λ ο (A)	Perfec Direct	t Fit	Aged	Proc S,QaS	essed SiC grit polished
Ti Kα	2.75	42±8%	42.0	212±3%		
Ca Ka	3.36			204	144	946±3%
Κ Κα	3.74	35		254±4%		
Ru La	4.85	35	34.7	173	172	1361±6%
Nb La	5.73	50	49.9	209		
Ρ Κα	6.16	57	56.8			
Si Ka	7.13	69	69.0	185	214	1805±9%
Continuum	7.9	92±9%	95.6			
		±3%		±2%	±2%	

Table 4.7 PET (002) Measured values of the 2-reflection fwhm w_{cc} (arc sec)

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Line	λ Perfect		Processed		
	(Å)	Direct	Fit	S,QαS	SiC grit polished
Τί Κα	2.75	0.203±3%	0.204		
Ca Ka	3.36			0.218	0.065±1%
Κ Κα	3.74	0.300			
Ru La	4.85	0.441	0.443	0.192	0.041±2%
Nb La	5.73	0.464	0.463		
Ρ Κα	6.16	0.469	0.471		
Si Ka	7.13	0.441	0.441	0.185	0.027±4%
Continuum	7.9	0.392±2%	0.411		
		±1%		±2%	

Table 4.8 PET (002) Measured values of the 2-reflection peak reflection $\Pr_{\rm CC}$
λ 0 (Å)	Absorption Correction	Major Gaussian fwhm (arc sec)	Minor Gaussian fwhm (arc sec)	Ratio l	Ratio 2	^w c (arc sec)	Pc
2.75	2.4	9.865	50	0.8	0.2	26.9	0.334
4.85	1.25	4.765	50	0.95	0.05	21.8	0.575
5.73	0.75	7.10	50	0.95	0.05	32.7	0.415
6.16	0.88	7.55	50	0.95	0.05	38.5	0.368
7.13	0.89	3.60	50	0.95	0.05	43.3	0.523
7.9	1.20					63.3	0.609
1	l		I				

Table 4.9 PET (002) Fit parameters and characteristics of the fit line spread function.

[Nb Lα λ5.73			Si Kα λ7.13			
Surface Treatment	R _{cc} (radx10 ⁵)	wcc (arc sec)	Pcc	R _{cc} (radx10 ⁵)	cc (arc sec)	Pcc	
Untreated	18.9	133	0.24	25.1	164	0.26	
Sand blasting	30.4	843	0.053	26.8	956	0.036	
Steam blasting	16.0	235	0.123				
SiC polishing	38.1	884	0.054	30.5	928	0.040	

Table 4.10 PET (002) Measured characteristics for the surface treatments used to increase the Bragg reflection integral.







Figure 4.9 PET(002) 2-reflection fwhm



Figure 4.10 PET(002) 1-reflection resolution



Figure 4.11 PET(002) 2-reflection resolution





PET(002) 1-reflection peak reflection





Figure 4.13 PET(002) 2-reflection peak reflection



Figure 4.14 PET(002) 1-reflection fwhm for reflection orders n = 1 - 4



Figure 4.15 PET(002) 1-reflection resolution for reflection orders n = 1 - 4



Figure 4.16 PET(002) fwhm of the major Gaussian used in the fit



Figure 4.17 PET(002) fwhm of the minor Gaussian used in the fit



Figure 4.18 PET(002) The model lattice defect parameter

Notes on the theoretical modelling graphs

- In Fig.X.Y.la the 2-reflection fit function is represented by the full line and the measured (1,-1) rocking curve by the dotted line.
- 2. In figures showing the fit and Prins perfect lattice functions, the two functions are distinguished by the higher peak reflection of the Prins perfect lattice function. In the far wing regions (shown in the logarithmic plots), in cases where there is a difference, the fit function is higher than the Prins perfect lattice function.
- 3. $P_{\lambda}(\theta)$ and $P_{\lambda}(\beta)$ refer to 1- and 2- reflection functions respectively.















































(c) $P_{\lambda}(\theta)$, unpolarised radiation, calculated Prins perfect lattice and fitted functions

Figure 4.24.1 PET(002) $P_{\lambda}(\beta)$, $p_{\lambda}(\beta)$ calculated and measured, unpolarised radiation, λ 7.9





 $P_{\lambda\pi}(\theta)$ Prins perfect lattice and fitted calculated functions (c)



plotted with logarithmic ordinate



polarisation components, A 7.9 Ħ and D PET(002) $P_{\lambda}(\theta)$ Prins calculated and fitted, Figure 4.24.2



Figure 4.25 PET(002) A comparison of (1,-1) rocking curves of surface treated and untreated samples at 5.73 Å

CHAPTER 5

CHARACTERISATION OF ETHYLENEDIAMINE D - TARTRATE (020)

5.1 Introduction

Ethylenediamine d-tartrate (EDdT, $C_6H_{14}N_2O_6$, 2d = 8.797A) is a useful analyser for the 3 - $^{\circ}$ Soft X-ray region in that it is possessed of moderate reflection efficiency and large specimens of good chemical uniformity can be grown. EDdT (020) has approximately the same 2d spacing as PET (002) and in fact these two analysers complement each other for studies in the above wavelength region; the calculated reflection efficiency of EDdT is some 40% down on that of PET (see Figs. 4.3, 5.2.) whereas the calculated resolving power of EDdT is approximately 60% higher than that of PET (see Figs. 4.10, 5.10). EDdT does not cleave along the (020) plane and therefore has reflecting properties that depend on sample preparation. In view of the high potential resolving power of EDdT and the obvious application to spectral studies it is useful and interesting, to determine as part of a full characterisation, whether or not currently manufactured samples fully exhibit this crystal characteristic and if so, the stability thereof.

Several brief studies of EDdT have been made previous to this study. These include, the pilot study precursory to this work by Leigh,^{*s*} and sample preparation studies (through the observation of rocking curve profiles) by other workers.^{(of,110,111} The above studies will be referred to during the course of this more comprehensive study.

5.2 Data Sources and Details of Numerical Evaluation

All crystallographic data was obtained from Ref.112. The anisotropic temperature parameters given in this reference were employed in the crystal calculations. Since, as for PET, the constituent atoms of EDdT are low Z elements and the photon energies of the Bragg reflection region are much higher than the absorption edge energies of these atoms then it was appropriate to use Honl's formulae for calculation of anomalous dispersion terms. Expressions (1.21n), (1.21o) were evaluated for all K-shell orbitals in EDdT. Details of atomic scattering factor and linear absorption coefficient calculations are given in Section 4.2.

5.3 Bragg Dispersion Function

In view of the large temperature uncertainties incurred in the measurement of the Bragg dispersion function it was decided that no further measurements should be made until an appropriate crystal temperature control and monitoring system is installed into the instrument. Nevertheless a plot of calculated $\Delta\theta$ (λ) is shown in Fig. 5.1 and literature values of d₁₈ and α are as follows:

5.4 Line Spread Function Measurements

5.4.1 The Bragg reflection integral

a. Comment on the calculated results

The main point of interest in the calculated results is that apart from the lower R_c for EDdT the results for EDdT and PET have the same general form. Again the Darwin zero-absorption result is everywhere quite close to the Prins result due to the



Figure 5.1 EDdT(020) The s

The shift of P $_{\lambda}(\theta)$ from the simple Bragg angle (θ_{B}) due to dispersion

unit cell absorption cross section being everywhere less than the corresponding scattering cross section and correspondingly the Darwin zero-extinction function is everywhere much larger than the Prins result. The Darwin zero-absorption result is, however, further removed from the Prins integral particularly at higher wavelengths than for PET and as a result the ratio of the Darwin zero-extinction to Prins integral is lower. At 7^{A} the ratio is 3 and at 1^{A} it is 80. Calculated results for higher orders are shown in Fig. 5.6. The higher order results are over an order of magnitude down on the first order result so that contamination of reflected first order radiation by reflected higher order radiation will normally be small.

b. Measurements

Bragg reflection integral measurements for fresh and aged material were made using the asymmetric 2-reflection configuration with a rubidium acid phthalate monochromator, at wavelengths where the uncertainty on the polarisation correction is large. At wavelengths where this uncertainty is small, R_c values were derived from (1, - 1) parallel configuration R_{cc} measurements. All processed material R_c values were derived from R_{cc} measurements in order to avoid executing the excessively broad scans characteristic of the asymmetric 2-reflection configuration for such material. A mosaic polarisation correction can be applied with confidence at all wavelengths for the processed material. All results presented below have been corrected for polarisation bias incurred in 2-reflection measurement methods.

i. Perfect material Two samples of solution grown EDdT , cut and solution polished to the 020 planes were obtained.[†] The samples

[™] Manufactured by: Quartz et Silice, Samples 5044, 5045. Supplied by: Nuclear and Silica Products Ltd.

were stored , prior to use, in sealed desiccated plastic sachets and during the course of the measurement programme the samples, when not in use, were stored in a silica geldesiccator. Results of R_c and R_{cc} measurements together with measurement uncertainties are given in Tables 5.1, 5.2 and are shown by filled circles in Figs. 5.2, 5.3. The measured values are everywhere close to the Prins result, a good indication that the lattice structure of the perfect material is close to the Prins perfect lattice model.

<u>ii. Aged material</u> A study of the effects of sample aging on $\frac{R_c}{C}(\lambda)$ was made using a sample⁺ which had been employed occasionally over a period of about 5 years and had received considerable exposure to the laboratory atmosphere during that time. The results of R_c and R_{cc} measurements are indicated by open circles in Figs. 5.2, 5.3 respectively. The change in the R_c result is quite small, especially when compared with the effect of aging in PET. The largest measured change in R_c was found, as expected, at the shortest wavelength employed, 2.75Å, where the zero-extinction to perfect lattice limit R_c ratio is high. Even at this wavelength R_c had only increased by factor 1.25. This indicates that, with regard to normal laboratory usage and storage, EDdT is not very susceptible to chemical attack and that its crystal lattice structure is quite stable.

iii. Sample spread of characteristics. The above results show that the R_c characteristic of EDdT changes little with sample aging and therefore once a given sample has been calibrated its R_c (λ) result can be used with confidence for several years thereafter.

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Quartz et Silice Sample B

<u>iv.</u> Processed material. In spite of the small increment in $R_c(\lambda)$ with sample aging, the large difference between the zero-extinction and perfect lattice limits suggests that sample reflection efficiency can be substantially increased by inducing mosaic character using a surface damage technique. Following the success obtained with PET (see Section 4.4.1), a sample of EDdT was polished with SiC grit No. 220. The results are shown as filled squares in Figs. 5.2, 5.3. The improvement in the reflection efficiency is dramatic. The increase over the perfect material is by factor 2 at $6\hat{A}$ and by factor 6 at 2.75 \hat{A} with less than factor 2 to reach the zero-extinction limit.

c. The polarisation ratio

At each of four wavelengths R_{cc} and R_{c} for a perfect sample were measured by the symmetric (1, - 1) method and the dispersive asymmetric method respectively. The polarisation ratio $k\left(\theta_{B}\right)$ was then calculated at each pair of R_{cc} , R_{c} values using Eqn. (2.44). The measured values of R_{cc}/R_{c} (θ_{B}) and k(θ_{B}) are shown on Figs. 5.4, 5.5 respectively as filled circles. Uncertainties on the measured values are shown by error bars. Figures 5.4, 5.5 show that at $\theta < 45^{\circ}$ the measured result is quite close to the Prins result. This was also found for PET (002) and in Paragraph 4.4.1.c was accounted for in terms of the penetration of the incident beam below the surface layers such that reflection occurs in the bulk of the crystal which is well described by the Prins perfect lattice model. At $\theta > 45^{\circ}$ the measurement uncertainties are too large to allow unequivocal comment on the trend of the measured result but there is a suggestion that measured values are close to the Prins result at long wavelengths. Further comment is made in the discussion to follow.

<u>d. Discussion</u>. The close agreement between all calculated and measured results for perfect material gives confidence in the calculation and measurement methods. It is sometimes found in other analysers that although there is quite good agreement in the R_c (λ), R_{cc} (λ) results, there is a shift towards the zero-extinction limit in the R_{cc}/R_c, k results at longer wavelengths. The trend of the long wavelength results for EDdT is rather masked by measurement uncertainties, but there is no strong evidence of such a shift. This indicates, taking into consideration the lower penetration at long wavelengths, that the lattice structure of the measured EDdT sample is near to the perfect lattice limit even in the surface layers. This accords with the measured R_c (λ) result given above.

The most interesting feature of the results is the fact that although the calculated $R_c(\lambda)$ ratio for the zero-extinction to perfect lattice limit is large, only a small increase in $R_c(\lambda)$ due to sample aging was observed. This shows that EDdT suffers little damage from exposure to the laboratory atmosphere or from occasional usage as a Bragg analyser. Consequently the spread, in the $R_c(\lambda)$ characteristic of samples which have undergone varying degrees of aging, will be small. Nevertheless moderately severe damage to the crystal surface, such as that produced by the polishing technique described, causes large increases in $R_c(\lambda)$ thus revealing the magnitude of the above calculated ratio. It can be expected therefore that samples which have undergone different surface abrasion processes will exhibit a large sample spread in the $R_c(\lambda)$ characteristic.

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Line	λ ο (A)	Perfect Direct Fit		Aged	Processed †
Ti Ka	2.75	† 3.7±8%		+ 4.6	21.7
Κ Κα	3.74	4.5	3.93		
Ru La	4.85	4.7	4.35	5.3	12.2
Nb La	5.73	5.0	4.80		
РКа	6.16	5.6 ⁺	5.01	5.8 ⁺	10.0
Si Ka	7.13	7.7	7.84		
Α1 Κβ	7.96	14.0	14.6	14.4	15.5
		±5%		±5%	±10%

Table 5.1 EDdT (020) Measured values of the Bragg reflection integral R_c (radx10⁵)

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+ Result derived from $\rm R_{cc}$ measurement. All other results are derived from $\rm R_{ab}$ measurements.

Line	λ 0 (A)	Perfect Direct Fit		Aged	Processed
Ti Ka	2.75	3.8±8%		4.7	22.2
Κ Κα	3.74	4.5±9%	4.21		
Ru La	4.85	5.7	5.68	7.5	16.9
Nb La	5.73	9.3	8.51		
РКа	6.16	11.2	9.99	11.6	20.0
Si Ka	7.13	12.5	11.5		
А1 КВ	7.96	15.5±5%	16.0	14.8±7%	17.6±5%
		±3%		±5%	±10%

Table 5.2 EDdT (020) Measured values of the 2-reflection integral R_{cc} (radx10⁵)

Key to summary graphs



* For $R_{c}(\lambda)$

•	Measured	value	derived	from	R _{ab}	measurement

Measured value derived from R $_{\rm cc}$ measurement





118010 01








Figure 5.6 EDdT(020)

Bragg reflection integral for reflection orders n = 1 - 4

5.4.2 The function

a. Measurements

i. Perfect material. A study of $P_{\lambda}(\theta)$ was made by means of a series of (1, - 1) rocking curves for a pair of freshly supplied samples. A preliminary study showed that rocking curves were very sensitive to the size of the crystal surface reflecting area. This is clearly seen in Fig. 5.7 which shows the variation of w_{cc} with the aperture of the slit (slit 3, see Fig. 3.2) controlling the beam size at crystal B. Reduction of the slit aperture at a given wavelength lowers the measured w_{cc} such that the latter approaches the perfect lattice value.[†] This is illustrated by the measurements made at λ 5.73A where a reduction in slit aperture width from 4mm to 0.4mm reduces w_{cc} by factor 3. It is thought that the high w_{cc} at large aperture settings is due to undulations in the lattice planes which arise from bending strain and general disorders in the crystal lattice. If it is assumed that the pitch of the undulations is of the same order of magnitude as the dimensions of the larger reflecting areas employed then, in reducing the slit aperture, only a small region within the pitch of an undulation reflects the incident beam and thus the Bragg condition is fulfilled over a small range of crystal aspect angle. This is of course a simple-minded interpretation of the observed phenomenon since crystal lattice disorders are far more complex than is suggested here. It would appear in any case that the pitch of the disorder is macroscopic (i.e. of the order of millimeters) rather than microscopic (as found for example in mosaic structure) for if the latter were the case w_{cc} would be fairly insensitive to the slit aperture variations used in this study.

¹ It was found (as illustrated in Fig. 5.7) that excessive clamping pressure used in mounting the crystal increased the measured w due to induced bending strain. The crystal was therefore clamped as lightly as possible.

For a given slit aperture setting the factor which the measured w_{cc} is above the perfect lattice result is greater at short wavelengths than at long wavelengths. There are several reasons for this. The larger crystal surface reflecting area arising from the low glancing angle at a short wavelength results in further rocking curve distortion due to the effects discussed above which are æsociated with reflecting area size. At short wavelengths the perfect lattice w_{cc} is small and therefore any lattice defect will have a proportionately larger effect than at longer wavelengths where w_{cc} is greater. It should also be noted that for a given slit reduction the factor by which $w_{_{\rm CC}}$ decreases is greater at shorter wavelengths than at long wavelengths. This is because for a given reduction, say x, in the slit width the illuminated crystal surface area is reduced as a function of $\mathbf{X}/\sin \theta$, and since the defect density is low, at short wavelengths (small θ) there is a greater reduction in the effective defect density in the illuminated area than at long The result of an earlier EDdT study in this wavelengths. laboratory by Leigh is shown as upright crosses in Fig. 5.7. It would appear from the result that the problem of reflecting area size was not tackled in that study.

Since distortion-free (1, -1) rocking curves were required in the present study it was necessary to reduce slit apertures in order to minimise the above effects. Unfortunately, the extent to which the slit apertures could be reduced was limited by beam count rate losses and also the necessity to keep the horizontal angular intensity distribution $h(\alpha)$ as broad and uniform as possible in order to minimise distortion of the (1, -1) rocking curve (see Subsection 2.2.2.e.ii). The value of w_{cc} for the smallest slit

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apertures are shown as asterisks in Fig. 5.7. Even for this aperture setting, the measured w_{cc} result is not as close to the perfect lattice result at short wavelengths as it is at longer wavelengths which indicates that the effect of the above disorder is not entirely removed. Nevertheless the general trend of the measured and calculated results is very similar and in any case Fig. 5.7 shows that at $\lambda > 3.74$ [°] the use of smaller slit settings would produce little or no further reduction in w_{cc} . After optimisation of the slit aperture settings the lattice tilts were aligned at $\lambda 4.85$ [°]. The selection of this wavelength for the alignment was based on the criterion that although w_{cc} is smaller at shorter wavelengths the counting statistics at the chosen wavelength were much better.

In the study of the perfect material, the slit settings indicated by asterisks in Fig. 5.7 were used at λ 2.75, 3.74, 4.85Å : at longer wavelengths larger slit settings were used since, provided the increment was not too much, this introduced no further distortion into the (1, -1) rocking curve. The larger settings allowed a higher beam count rate and maintained the horizontal angular intensity distribution greater than w_{cc} . A study of the main body and wings of each rocking curve was made as described in Section 3.4. Measured values of w_{cc} , $(\Delta\lambda/\lambda)_{cc}$, P_{cc} for perfect material are shown as filled circles in Figs. 5.9, 5.11, 5.13 respectively and w_{cc} , P_{cc} values are listed in Tables 5.3, 5.4 together with measurement uncertainties. Comment and explanation concerning the discrepancy between measured and calculated Prins perfect lattice result at short wavelengths is given above. At $\lambda \ge 5A$ the measured and calculated results follow a very similar trend. Nevertheless, the measured result is some way from the calculated result; approximately 25% above in the case of

the w_{cc} result. This difference is not related to the size of the reflecting area since the results obtained for smaller areas were identical. It would appear that even after the manufacturers surface preparation by solution polishing, a small degree of mosaicity remains. Even so, as mentioned in the discussion to follow the results compare favourably with those of other workers.

The measured and calculated results for the perfect material were sufficiently close to justify an attempt to fit the selfconvolution of the Prins function to the (1, -1) rocking curve. A fit to within a few percent of w_{cc} and P_{cc} of the (1, -1) rocking curve was obtained at all wavelengths apart from $~\lambda 2.75 {\hbox{\AA}}$. At that wavelength the large perturbation of the Prins function required to obtain a fit to w_{cc} and P_{cc} produced a poor fit to the overall shape of the (1, - 1) rocking curve. In any case the large perturbation required at this wavelength renders the fit procedure invalid. The parameters used to obtain a fit at the other wavelengths are listed in Table 5.5. and the widths of the major and minor Gaussian spread functions are plotted in Figs. 5.16, 5.17 respectively. Figure 5.13 shows that at 3.74, 4.85Å the Prins P result is well above the measured result and consequently an absorption correction was required in the fit procedure at these two wavelengths. At all other wavelengths only the two Gaussian spread functions were required to obtain a fit. The fwhm of the major Gaussian spread functions is a small fraction of that of the Prins function at all wavelengths thus showing that only a small perturbation of the Prins function was required to obtain a fit. The most interesting feature of the fit parameters is the trend in the widths of the major and minor Gaussian functions towards higher values with increasing wavelength. This result is to be expected on the basis that at longer wavelengths the penetration depth is smaller so that greater

spreading of the Prins function is required in order to model the effect of surface damage upon the perfect crystal line spread function. Conversely at short wavelengths the incident beam penetrates further into the crystal so that a greater proportion of the beam is reflected by the more uniform layers below the surface. Since the reflection behaviour of these lower layers is well described by the Prins model, only narrow Gaussian spread functions are required to obtain a fit to the measured rocking curve. It should also be noted that, in accordance with the discussion given in Subsection 2.2.2, the minor Gaussian function makes a small contribution to the total spreading of the Prins function. Figures 5.18.1a, 5.23.1a present for each wavelength a linear plot of the fit to (1, - 1) rocking curve superimposed on the rocking curve. The 2-reflection perfect lattice fit function is shown by the continuous line and the (1, -1)rocking curve by the stepped line. Logarithmic plots of these curves are shown in Figures 5.18.1b, 5.23.1b with measured points obtained from the (1, - 1) rocking curve wing studies shown as dots. In all cases the fit obtained is good to 2 or 3 orders of magnitude down on P_{cc} . Unfortunately, the rather low count rates obtained with the small slit settings did not allow accurate measurement in the extreme wings of the rocking curves.

The parameters w_c , $(\Delta\lambda/\lambda)_c$, P_c of the perfect lattice fit function are shown as filled circles in Figs. 5.8, 5.10, 5.12. The fit w_c , $(\Delta\lambda/\lambda)$ results follow the trend of the Prins results at all wavelengths and as expected from previous experience with PET the fit result is about 25% above the Prins result which is the same amount by which the rocking curve characteristics are above the 2-crystal Prins result. This feature also characterises the P_c result as may be seen by comparison of Figs. 5.8, 5.9., consequently the trend towards a larger difference between the measured and Prins P_{cc} results at short wavelengths is in evidence in the fit and Prins P_{c} results. On the basis of the above results the fit function parameters obtained at each wavelength were regarded as a good approximation to those of the perfect material line spread function.

Plots of the fit and perfect lattice functions for σ -, π -polarised and unpolarised radiation are presented in Figs. 5.18 - 5.23. In all cases the curve of lower peak value is the fit function. The most striking feature of these plots is that the characteristic asymmetry of Prins perfect lattice function is not seen in the fit function at any wavelength. This indicates that although the required perturbation to the perfect lattice function is not large, it is sufficient to mask the shape of this function. It would appear that the fit procedure has been rather 'stretched' and that although the parameters of the fit function are reasonable, it is probable that the shape of the fit function does not fully describe that of the perfect material line spread function.

<u>ii. Aged material</u>. A description of the aged sample is given in Subsection 5.4.1. Measured values of w_{cc} , $(\Delta\lambda/\lambda)_{cc}$ and P_{cc} are shown as open circles in Figs. 5.9, 5.11, 5.13 respectively. At long wavelengths there is little difference between the aged and perfect material values. The trend towards a greater difference between the aged and perfect material results at short wavelengths is similar to the trend found between the perfect material and perfect lattice results. This suggests that undulations in the lattice of the aged sample are causing a deceptively high w_{cc} at short wavelengths. Since the slit aperture settings were already very small it was not possible to prove the above point by reducing them further. Taking the high w_{CC} values at short wavelengths into consideration the aged material result is very much in accordance with the results of R_{C} measurements i.e. the effects of aging upon the line spread function of EDdT are small.

iii. Sample spread of characteristics. The perfect material results show that over most of the Bragg reflection wavelength range the (1, - 1) rocking curve of EDdT is susceptible to distortion associated with undulations in the crystal lattice, therefore all discussion of the sample spread of characteristics must be given in the light of this fact. The slit apertures used in this study eliminated distortion at long wavelengths and results indicate that for this wavelength range and experimental condition a group of samples which have undergone varying degrees of aging may be expected to have a small spread of characteristics. In the short wavelength region distortion of the (1, -1) rocking curve was so severe that not even the very small slits used were able to completely eliminate this effect. Results show that for given slit aperture settings the sample spread of characteristics is large and thus before using a given sample as an analyser, calibration is required with great attention paid to factors such as the reflecting area size and the clamping pressure required to mount the sample for if the latter is excessive then bending strain will be introduced into the crystal lattice.

<u>iv.</u> Processed material. A comparison of the effect of various abrasion techniques upon the (1, -1) rocking curve for the case of PET is given in Subsection 4.4.2. The surface of a sample of EDdT was abraded using the chosen SiC grit abrasion technique. All the (1, -1) rocking curves of this processed sample were well formed and near-Gaussian in shape. Measured values of w

 $(\Delta\lambda/\lambda)_{CC}$, P are shown as filled squares in Figs. 5.9, 5.11, 5.13 respectively. The results show that the abrasion process has produced an increase in $R_{c}(\lambda)$ above the perfect material result (see Subsection 5.4.1) at the expense of an order of magnitude loss in resolution. The apparent absence in the results of low angle distortion of the (1, -1) rocking curve indicates that this effect has been completely masked by the large mosaic spread of the sample domains. The w_{cc} (λ) and P_{cc} (λ) results are highly wavelength dependent. Indeed the processed material $\boldsymbol{P}_{_{CC}}$ ()) result is considerably more wavelength dependent than the perfect material result. This is possibly due to the fact that the low extinction characteristic of the sample allows full advantage to the short wavelength X-rays to penetrate further into the crystal than the softer long wavelength X-rays, consequently the short wavelength X-rays are reflected by the more uniform crystal lattice below the surface.

b. Discussion

The perfect material $w_{cc}(\lambda)$, $(\Delta\lambda/\lambda)_{cc}(\lambda)$, $P_{cc}(\lambda)$ results are quite close to and follow the trend of the calculated results, except at short wavelengths for reasons given above. Once again this confirms that the methods of calculation and experiment are free of gross error. The measured results are not as close to the calculated results as is found for PET (at long wavelengths) and ADP which indicates that there is still some room for improvement in sample preparation. Nevertheless the results compare favourably with those of other workers. The small reflecting area used in this study provides a resolving power $(\Delta\lambda/\lambda)_c \approx 1.2 \times 10^{-4}$. Burek et al, for admittedly larger reflecting area (100 cm²), obtained a resolving power $\approx 4 \times 10^{-4}$. Both these values need to be compared with the potential resolving power $\approx 1 \times 10^{-4}$. It is interesting to note that Burek et al 183

mention that 'Unzicker and Meekins have obtained large samples of EDdT whose rocking curves were so narrow that the crystals must be nearly perfect'.

Although the difference, 25%, between the perfect material and calculated results is not gross; it is sufficiently large, in view of the results of the fit procedure, for one to question the validity of fit for this case. It is noted in Paragraph i. above that the parameters w_c , $(\Delta\lambda/\lambda)_c$, P_c of the fit line spread function seem reasonable but nevertheless the perturbation required in the fit procedure is sufficiently large to produce a fit function which is quite different in shape from the Prins function.

The aged material study showed that under normal laboratory conditions EDdT shows small change in $w_{cc}(\lambda)$, $P_{cc}(\lambda)$ with sample age. This accords with the results of Burek et al who found that their perfect material $w_{cc}(\lambda)$ result was stable even after exposing a sample to a 100% humidity atmosphere for a day and to large radiation doses.

A comparison of Figs. 5.2, 5.9 shows that the SiC grit abrasion method may be used to greatest effect at short wavelengths. The loss in resolution incurred in this technique is everywhere an order of magnitude down on the perfect material but the gain in reflection efficiency is much greater at short wavelengths than at long wavelengths. From a comparison of the perfect and processed material results it can be concluded that within the limitation of producing well-formed rocking curves then one can expect a considerable spread in the rocking curve parameters for various surface damage processes.

Line	λ (Å)	Per Direct	fect Fit	Aged	Processed
Ti Ka	2.75	15±13%		22	141
К Ка	3.74	17±12%	17.0		
Ru La	4.85	23±3%	23.4	27±5%	327
Nb La	5.73	32±6%	32.1		
РКα	6.16	39±7%	38.6	41	506
Si Ka	7.13	52±4%	52.0		
А1 КВ	7.96	76±8%	75.4	91	700±22%
				±9%	±9%

Table 5.3 EDdT (020) Measured values of the 2-reflection fwhm w_{cc} (arc sec)

Line	λ (Å)	Perfect Direct Fit		Aged	Processed	
Ti Kα	2.75	0.40		0.31	0.14	
Κ Κα	3.74	0.39	0.399			
Ru La	4.85	0.38±2%	0.381	0.38	0.041	
Nb La	5.73	0.42	0.415			
Р Ка	6.16	0.43±6%	0.418	0.41	0.029	
Si Ka	7.13	0.35±2%	0.352			
Α1 Κβ	7.96	0.33	0.336	0.26±6%	0.019±11%	
		±4%		±3%	±4%	

Table 5.4 EDdT (020) Measured values of the 2-reflection peak reflection $\mathop{}_{\rm CC}^{\rm P}$

λ (Å)	Absorption Correction	Major Gaussian fwhm (arc sec)	Minor Gaussian fwhm (arc sec)	Ratio 1	Ratio 2	^W c (arc sec)	Pc
3.74	1.0	3.0	25	0.95	0.05	11.1	0.603
4.85	0.5	3.625	45	0.95	0.05	14.7	0.496
5.73		5.0	90	0.95	0.05	21.0	0.386
6.16		6.5	160	0.97	0.03	26.1	0.330
7.13	Т. Т.	8.0	1 30	0.97	0.03	32.7	0.403
7.96		11.0	180	0.98	0.02	48.6	0.505

Table 5.5 EDdT (020)

Fit parameters and characteristics of the fit line spread function

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Figure 5.8 EDdT(020) 1-reflection fwhm



Figure 5.9 EDdT(020) 2-reflection fwhm





1-reflection resolution



Figure 5.11 EDdT(020) 2-reflection resolution





1-reflection peak reflection





EDdT(020) 2-reflection peak reflection



Figure 5.14 EDdT(020)

1-reflection fwhm for reflection orders n = 1 - 4



Figure 5.15

EDdT(020)

l-reflection resolution for reflection orders n = 1 - 4



Figure 5.16 EDdT(020)

fwhm of the major Gaussian used in the fit



Figure 5.17

fwhm of the minor Gaussian used in the fit

Notes on the theoretical modelling graphs

- In Fig.X.Y.la the 2-reflection fit function is represented by the smooth line and the measured (1,-1) rocking curve by the stepped line.
- 2. In Fig.X.Y.1b the 2-reflection fit function is represented by the full line and the measured points of the (1,-1) rocking curve are represented by dots.
- 3. In figures showing the fit and Prins perfect lattice functions, the two functions are distinguished by the higher peak reflection of the Prins perfect lattice function. In the far wing regions (shown in the logarithmic plots), in cases where there is a difference, the fit function is higher than the Prins perfect lattice function.
- 4. $P_{\lambda}(\theta)$ and $P_{\lambda}(\beta)$ refer to 1- and 2-reflection functions respectively.



 $P_\lambda(\theta)$, unpolarised radiation, calculated Prins perfect lattice and fitted functions (c)

25°10′00″

25 09 30"

(c) plotted with logarithmic ordinate as (p)

25°11'00"

25'10'00"

25°09'00"

 $P_{\lambda}(\beta)$, $P_{\lambda}(\theta)$ calculated and measured, unpolarised radiation, λ 3.74 EDdT(020) Figure 5.18.1







(a)



(c)







(a)



(c)


























(a)



(c)





CHAPTER 6

CHARACTERISATION OF AMMONIUM DIHYDROGEN PHOSPHATE (101)

6.1 Introduction

Ammonium dihydrogen phosphate (ADP, $NH_4 H_2 PO_4$, 2d = 10.64 Å) has found wide application in X-ray spectroscopy by virtue of its moderate reflection efficiency and high resolving power and because large high quality samples may be easily produced on a commercial scale. The (101) lattice planes of ADP are particularly useful in solar atmosphere spectral studies because the lattice period allows ADP (101) to be used to measure the spectrum to a little longer than 10\AA . This latter is important in that a strong and diagnostically useful multiplet of the He - like spectrum of Mg XI lies at 9.1 - 9.3Å. Because these lines lie just outside the 2d range of most other similar analysers, ADP(101) has been much favoured for spectral measurement of the solar atmosphere. High quality spectra, using ADP(101), have been available for some years 115,11 but interpretation of these spectra has been impeded by the lack of knowledge of R $_{\rm c}$ (λ) for ADP (101). Deslattes et al¹¹⁶ offer helpful comments concerning $R_{c}^{(\lambda)}$ as do Burek et al, though neither offers numerical values. Burek¹¹⁰ gives calculated predictions but these are not supported by measurement. Parkinson¹¹⁷ and Pye et al¹¹ both quote unpublished values by Evans and Leigh, which values were found during preliminary explorations prior to the work reported below. A clear intention of the undertaken study was to obtain $R_{c}(\lambda)$ as part of full characterisation of ADP(101) in order to allow retrospective interpretation of existing published solar atmosphere spectra, and to provide this information for the benefit of new measurements, including NASA's Solar Maximum Mission.

ADP does not cleave along the (101) lattice planes and therefore reflection properties are dependent on sample preparation. Deslattes et al report that large highly perfect single crystals of ADP can be grown from solution and that after cutting to the desired planes samples can be restored to perfection by solution polishing. There is some debate (details of which are given in the final discussion of results) as to the long term stability of perfect sample reflecting properties and therefore a useful contribution to this debate was sought in the investigation to follow.

6.2 Data Sources and Details of Numerical Evaluation

Crystallographic data including anisotropic temperature parameters were taken from Ref.119. It was necessary to use a method more powerful than Hönl's, for calculating the frequency dependent terms of f_i (20,k) for the reason that since the contributions arising from the L-shell electrons of phosphorous could not be neglected then the requirement for Hönl's method that the electrons may be approximated by hydrogenic wavefunctions is not met. Resort was made therefore to the methods of Parratt and Hempstead and of Cromer and Liberman. Preliminary calculations of reflection characteristics showed that outside the immediate vicinity of the PK edge region $(5.5 - 6.0 \text{ \AA})$ (which neither method is sufficiently powerful to deal with) there was negligible difference between the results obtained from these two methods.[†] Therefore all calculated results presented here were derived using the simpler method of Parratt and Hempstead. Points of note concerning the implementation of this method are as follows. In spite of the fact that there is doubtful need to retain $\kappa_{\alpha} \neq 0$ (see footnote to Paragraph 1.3.2.c.ii) the classical value κ_q was used throughout. $f_i(2\theta,k)$ was calculated for each atom in ADP of for $1 < \lambda < 10.5$ Å (a cautionary note for wavelengths close to the PK edge is given at the end of this section) by using (1.27b), (1.27c), making

[†] Preliminary calculations were also performed using Hönl's method, the results of which showed a 5% difference (in the Prins characteristics) from the other methods in the 6-8Å region but were not sensibly different at longer wavelengths and below the PK edge.

summations as in (1.20) and then substituting f'_{oj} for Z as noted in Paragraph 1.3.2.c.ii. In making these calculations, values[†] of ω_q from Bearden and Burr¹²⁰ were used. For all K orbitals values n = 7, m = 8(i.e. $P_{K} = 2.75$) were used. For the phosphorous L_{I} orbitals values n = 2, m = 3 (i.e. $P_{L_{I}} = 2.33$) were used and for the L_{II} and L_{III} orbitals values n = 3, m = 4 (i.e. $P_{L_{II}} = P_{L_{III}} = 2.5$) were used. These values are recommended by various authors including Parratt and Hempstead,³⁷ Cromer³⁶ and Dauben and Templeton.³⁸ The K-electron oscillator strengths for H , N and 0 were calculated from James (Ref.21, Expression (4.60)) and K-, L_{I} , L_{II} , L_{III} electron oscillator strengths for P from Cromer.

Although Bragg reflection characteristics were calculated at all wavelengths in the range given above it was seen from the reflection integral measurements to follow that the power law assumption (1.26) is inadequate to predict characteristics at wavelengths to within a few percent of the phosphorous K edge. For this reason some figures have been left incomplete in the region 5.5 - 5.9Å and the reader is cautioned that within this region the calculated results are subject to large uncertainties. This matter will be discussed further in the course of this chapter.

6.3 Bragg Dispersion Function

For reasons given in Section 5.3 the Bragg dispersion function was not measured. A plot of calculated $\Delta\theta(\lambda)$, given in Fig.6.1, clearly shows that the enhanced anomalous dispersion at the PK absorption edge has a relatively small effect upon the general form of $\Delta\theta(\lambda)$. Literature values of d₁₈ and α are as follows:

d ₁₈ (Å)	$\alpha(x 10^4)$
5.3201±0.0006 ¹¹⁸	0.216
5.329	

⁺ Modifications of 'edge' frequencies due to effects of molecular and solid bonding were neglected. Though these modifications are often not precisely known it is possible to make usefully accurate theoretical estimates and it might have been better to use those. Their neglect allows (very slight) distortion of the calculated results presented.

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Figure 6.1 ADP(101) The shift of $P_{\lambda}(\theta)$ from the simple Bragg angle (θ_B) due to dispersion. The dotted line shows the contribution to $\Delta \theta$ from normal dispersion alone

6.4 Line Spread Function Measurements

6.4.1 The Bragg reflection integral

a. Comment on the calculated results

It is seen from Fig. 6.2 that for $\lambda < 2$ Å the Prins perfect lattice and Darwin zero-absorption results are quite close thus indicating that in this wavelength region the unit cell absorption cross section is much scaller than the corresponding scattering cross section. At longer wavelengths, particularly near the P K edge, the Prins result is well below the Darwin result. This is to be expected since the Darwin calculation takes no account of the enhanced unit cell absorption cross section associated with the P K edge. Correspondingly at short wavelengths the zero-extinction result is an order of magnitude above the Prins result but at longer wavelengths the two results are considerably closer. It should be noted that on the low wavelength side of the PK edge the zero-extinction result gradually approaches the Prins result but on the high wavelength side of the edge the zero-extinction result rises rapidly above the Prins result. This may be interpreted with the aid of Fig. 6.7 which shows that at $\lambda/\lambda_k < 1, \Delta f''$ and hence the unit cell absorption cross section increase steadily with increasing wavelength whereas at $\lambda/\lambda_k \sim 1$, $\Delta f''$ falls abruptly and so there is a correspondingly decrease in the absorption cross section. Since the zero-extinction result is a function of μ_{ρ} it is much more sensitive than the Prins result to changes in the absorption cross section so that the fall in Δf " at the edge will cause a larger increase in the former result than the latter.

b. Measurements

Except where noted, all measurements reported below were made by the dispensive asymmetric configuration 2-reflection method using rubidium acid phthalate(001) as the monochromator. The results graphed have been corrected for the (small) residual polarisation bias that remains even with this method.

i. Perfect material. Several samples of solution grown ADP crystals were obtained.[†] These samples had been sawn and solution polished to expose the (101) planes. They were carefully handled, shipped and stored prior to use and contained in sealed desiccated sachets. The results of measurements of R_{c} (λ) made by the dispersive asymmetric configuration 2-reflection method are shown by the filled circles in Fig. 6.2. Measurement of $R_{_{\rm CC}}$ (\lambda) , (the results of which are shown by filled circles in Fig. 6.3) allows evaluation of the polarisation coefficient $R_{c\pi}(\lambda)/R_{c\pi}(\lambda) = k(\lambda)$ (see below). In order to determine k(λ) efficiently, R_{c} , R_{c} were measured chiefly at wavelengths where the uncertainty on k (λ) is high i.e. at $\theta \simeq 35^{\circ}$ and 55° (see Subsection 2.2.1.b). Once the function $k(\lambda)$ is available it is then possible to make further measurements of $R_{c}(\lambda)$ by the alternative method of use of the symmetrical non-dispersive (1, - 1) 2-reflection configuration (see Subsection 2.2.1.b). Some additional values of $R_{c}(\lambda)$ found by this method are also included in Fig. 6.2, distinguished as filled triangles. The final characteristic determined as a best fit to these 2 sets of data points is shown as the medium full line on Fig. 6.2. The net uncertainty on this characteristic embracing both systematic and random effects is about 5%. Fuller details of measurement uncertainties are given in Table 6.1. From Fig. 6.2. it is noted that, as can be expected, the effects of anomalous dispersion and absorption by the phosphorous K-shell electrons are very significant to the values of $R_{c}(\lambda)$ in the

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⁺ Quartz et Silice, Samples 992,993

immediate neighbourhood of the phosphorous K edge. In this neighbourhood the variation of $R_{c}(\lambda)$ is too rapid for economic definition of the function by the point by point method as described above. The 1-reflection scan method described in Subsection 3.4.4 was therefore implemented.[†] In the restricted interval 5.5 - 5.9Å the results of this method did not confirm the calculated predictions as in Fig. 6.2. The circumstances that give rise to this appear to be as follows. The standard texts, e.g. James (Ref. 21, p147, 155) give various approximate solutions for the integration of the semi-classical dispersion equation for the case where the absorption coefficient may accurately be taken as a power law with wavelength. It was clearly seen that those approximations progressively failed for photon frequency taken ever closer to the edge frequency. Parratt and Hempstead gave the exact integration for the general case of the power law assumption. This enables the scattering factors f_i (20, k) to be calculated continuously through the 'edge' frequency, without revealing a pole in the function, provided that some suitable approximation is chosen for the radiation damping constant. The computer programs used in the present calculations were developed to take advantage of this exactitude and, in part, were motivated by the intention to use them in this present calculation of the effect of the phosphorous K-edge on the diffraction behaviour of ADP. In the event, preliminary measurements reveal severe structure in the scattering factor of ADP near the phosphorous K-'edge' frequency which we interpret as due to resonance line scattering. Since this effect destroys the validity of the power low assumption within several percentage points of the

[†] Details of the evaluation of R_{c} (λ) from this method are given in Ref. 81, p.179.

'edge' frequency the algebraic exactitude of the Parratt and Hempstead integration is not helpful to this particular problem.⁺ The effect of resonance line absorption/scattering by oxygen atoms on the diffraction behaviour of KAP has been known for some years, e.g. Burek¹¹⁰, but this had been thought an exceptional case.⁺ In the light of present experience it may not be exceptional. It appears that at soft X-ray wavelengths, where the K-edges encountered are those of relatively low Z elements (and therefore outer orbitals are often unfilled right down to principal quantum number n = 3) resonance line absorption/scattering effects may be endemic. In this case, all calculations of Bragg diffraction properties which use simple functional representations of the frequency dependence of absorption coefficients should be regarded as unreliable within several percentage points of the nominal 'edge' frequency <u>unless they are</u> supported by careful measurements throughout that waveband.

At present, analysis of the results of the 1-reflection scan method is in progress using methods¹²² for the calculation of anomalous dispersion terms which are more powerful than those described in Chapter 1. A full report will be given when this work is finished. For the time being the author is obliged to leave Fig.6.2 incomplete for the waveband 5.5 - 5.9 Å, though outside this band the results are reliable within the limits specified. Until the above matters are cleared up it is recommended that ADP (101) diffractions should not be used for spectrometric work in this waveband. It is clear that the caution might well be extended to the use of other analysers at

⁺Parratt and Hempstead were themselves aware of the existence of resonance line scattering, as is clear from their paper. At the somewhat harder X-ray energies to which they directed their work they were more concerned with the indirect way in which the phenomenon affected the calculation (via the effect the resonances have in obscuring the correct choice of 'edge' frequency) rather than the direct effect on the scattering factor. It was noted from our preliminary work as above that the phosphorous K-'edge' in solid #ADP is about 7 e-volts above the value listed by Bearden and Burr¹²⁰.

Note that later in his paper (his Fig.21) Burek himself predicts a semiclassical dispersion shape, bereft of resonances, for the function $R_C^n(\lambda)$ for ADP in the neighbourhood of the phosphorous K-edge from his own Parratt and Hempstead calculation. He had no measured data to protect him from omission of the resonance effects. wavelengths near absorption edges of their constituents until they are carefully examined. The matter is of some importance. The effect in KAP became known only after a feature in KAP diffracted spectra of the solar corona had been erroneously assigned to a plasma emission line.¹²³ The feature was of course due to a spurious line-like enhancement of the continuum spectrum by the resonance scattering of oxygen atoms in the KAP lattice.¹²⁴ The spectra of natural plasmas near 10^7 K (e.g. solar flares) will be densely packed near 5 Å with emission lines from Li-like to 0-like iron and there will be serious risk of similar error arising from the same effect in ADP until the matter is clarified.

ii. Aged material Both Deslattes et al and Burek et al commented upon the tendency for the diffraction properties of ADP (101) to change significantly on exposure to the atmosphere, though neither gave quantitative data. During earlier studies in this laboratory on diffraction from the PET (002) and KAP (001) 40 planes, evidence was found for time changing of the behaviour of those lattices also, and quantitative descriptions were given. From the point of view of astronomical applications it is plainly important to have this information for ADP (101) also. Therefore several further samples which had been in routine use in our laboratories for about five year were examined. They had been much used (in vacuum) as diffraction analysers during that period, and so had received substantial radiation doses at their surfaces. During most of the periods of storage between usage they were exposed to the (undesiccated) local atmosphere. Their characteristic R_{c} (λ) functions had in fact been measured, by methods as above, when they were new with results indistinguishable from those of Paragraph i above for wavelengths longer than the phosphorous K edge, and results only slightly different at shorter wavelengths. Remeasurements were made after

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five years usage and $R_c(\lambda)$, $R_{cc}(\lambda)$ results are shown as the open circles on Figs. 6.2, 6.3 respectively. These values do not show much change compared with the values for the fresh stock, except at the shortest wavelength at which measurement was made (2.75Å), where there is an increase of 31%. This is just as is to be expected from examination of the calculated Darwin zeroextinction and Prins characteristics, cf Lewis, Maksym and Evans⁴⁰. Further comment relevant to this matter is added below.

iii. Sample spread of characteristics; flown samples. As noted above, two samples of ADP (101) produced five year apart, both (when fresh) showed characteristics barely distinguishable from that calculated, except at the shortest wavelengths. This was found to be the case also for several other fresh samples which have been examined over the years. However, in Tables 6.1, 6.2 the measured values of R_c (λ), R_{cc} (λ) respectively for two further samples of special interest are shown. These results are not shown because they lie too close to other points to be included there). These are the values for analysers recovered after observations † in space as extensively reported by Parkinson, Pye et al, and many other articles published and in the press, which refer to rocket serial numbers as indicated. Independent analysis of spectra published by these authors should refer to Table 6.1, (and use the graphs of Fig. 6.2 to guide interpolation) for the relevant calibration data. It is noted that these values are also not much different from those for fresh stock, except (again) at the shortest wavelength measured. It can be concluded that of a total of about eight samples studied, none differed by more than about 3% from the theoretical

 † On SKYLARK rocket vehicles, serial numbers 804, 1101, 1206.

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characteristic except for wavelengths below about 3.5Å, where there is a clear systematic trend for the values of $R_c(\lambda)$ to increase slowly with the age of the sample.

In the study of pentaerythritol iv. Processed material analysers, see Chapter 4, a means of substantially enhancing the reflecting power of the analyser was found 4 essentially by reducing both the primary and secondary extinction effects in the sample. In the present case there is less scope for achieving that end, at least at the longer wavelengths. It can be seen from Fig. 6.2 that the zero-extinction characteristic tends towards the perfect crystal limit at long wavelengths, so there is not much room for improvement. However, the SiC abrasion process was applied with results as shown by the filled squares on Figs. 6.2, 6.3. As can be expected from remarks made above there was substantial improvement in the efficiency at 2.75Å but some degradation in performance was found at the longer wavelengths. There is therefore doubtful value in attempts to improve the reflection efficiency of ADP (101) at long wavelengths.

c. The polarisation ratio

At each of three wavelengths the 2-reflection integral was measured by both the dispersive asymmetric method, and by the symmetric (1, -1) method. At each of these wavelengths the pair of values then allows of unique determination of k (θ_B) from the measurements alone by the use of Eqn. (2.44). The measured values of R_{cc}/R_c (θ_B) and k (θ_B) are shown on Figs. 6.4, 6.5 respectively as filled circles. Measurement uncertainties are indicated by error bars. Note that interpolation then allowed determination of values of k (θ_B) at certain other wavelengths for which the values of $R_c(\lambda)$ could be fixed from the symmetric (1, -1) measurements alone. The filled triangles in Fig.6.2 were fixed in this way. Figures 6.4, 6.5 show that apart from a small angular region just above the phosphorous K edge then the Prins perfect lattice and zero-extinction results are quite close. There is a tendency for the measured values to move closer to the zero-extinction limit with increasing $\theta_{\rm B}$. This was found and explained for PET(002) in Chapter 4.

d. Discussion

Figures 6.2-6.5 present results of a somewhat exhaustive study, both by calculation and measurement, of the first order Bragg response of ADP(101). The calculations have embraced three limiting cases, so that the separate effects due to a perfect lattice, due to anomalous dispersion and to absorption, and due to lattice disorders, can be seen. Measured data presented includes results for fresh and nearly perfect samples, used samples, samples recovered from space, and abused samples. The agreement of calculation with measurement is regarded as satisfactory, and this leaves little room for doubt as to the validity of either. The reader may use Figs. 6.2-6.5 for independent interpretation of published solar spectra obtained during the rocket flights indicated. It is also found that the spread of characteristics for different samples of ADP(101), at least supplied by the manufacturer indicated, is sufficiently small that others may use these data as calibrations of their crystals also, provided these are well cared for in the manner indicated. For users who fear confusions of their spectra by higher order diffractions from ADP(101), the calculated response, both for the perfect lattice and zero-extinction cases, for the first few orders are shown in Fig.6.6. Although these have not been checked by explicit measurement the calculations differ but trivially from those made for the first order as above, so that the convincing agreement achieved for that case leaves little room for these higher order results to be in error.

For interest, the reader should note that the integral response for a room temperature vibrating lattice, is depressed by only ~1% below that of a static lattice for first order reflections. The depression increases rather rapidly with order, though, and is ~20% in fourth order.

Line	λ (Å)	Perfect	Aged ⁺	Skyl Flight 1206	ark Samples ⁺ 804/1101	$Processed^+$
Τί Κα Κ Κα	2.75	$3.34^{+} \pm 1\%$	4.34	3.85	3.45	5.8 ± 8%
Ru La S Ka	4.85	3.53 ± 1% 2.9 ⁺	3.6	3.3		2.5
Nb La P Ka	5.73 6.16	2.1 ⁺ 3.5	3.7 ± 6%	3.5 ± 6%		3.5
Al Ka Mg KB	7.13 8.34 9.52	4.5 ± 2% 5.8 9.7 ⁺	5.9	5.5	5.4	4.4
		± 5%	± 3%	± 3%	± 3%	± 4%

Table 6.1 ADP(101) Measured values of the Bragg reflection integral R_c (rads x 10⁵)

⁺Result derived from R measurement. Other results are derived from R measurements.

Line	λ (Å)	Perfect	Aged	Skylark Flight Samples 1206 804/1101		Processed
Τί Κα Κ Κα	2.75	3.37 3.71	4.40	3.90	3.49	5.8 ± 8%
Ru La S Ka Nh La	4.85 5.37 5.73	3.98 3.74 3.0 + 4%	4.1	3.96		3.0
P Ka Si Ka	6.16 7.13	5.8	6.1	5.8		5.8
Al Ka Mg KB	8.34	10.5	10.6	9.9	9.8	7.9
		± 1%	± 2%	± 2%	± 2%	± 2%

Table 6.2 ADP(101) Measured values of the 2-reflection integral R_{cc} (rads x 10⁵)

Fit R and R results are identical to the Prins results shown in Figs.6.2 and 6.3

Key to summary graphs

	Darwin zero-absorption limit
	Darwin zero-extinction limit
	Prins perfect lattice limit
entritoretonomen 🖗 essencesaria	Perfect material*
0	Aged material
•	Processed material - SiC grit polished
	Skylark 804/1101
∇	Skylark 1206

* For $R_c(\lambda)$

Measured value derived from R_{ab} measurement

 Measured value derived from R_{cc} measurement



Figure 6.2

ADP(101)

Bragg reflection integral



Figure 6.3 ADP(101) 2-reflection integral







Figure 6.6

ADP(101)

Bragg reflection integral for reflection orders n = 1 - 4



 $\Delta \texttt{f'}$ and $\Delta \texttt{f''}$ are calculated by Parratt and Hempstead's method

6.4.2 The function

a. Measurements

i. Perfect material Two fresh ADP samples were used to generate (1,-1) rocking curves at selected emission line wavelengths in the Bragg reflection wavelength range. A preliminary study showed that at short wavelengths the rocking curve fwhm was extremely sensitive to the size of the width of the beam incident on the crystal faces. This is clearly illustrated in Fig.6.8 which shows that at 2.75 Å reduction in Slit 3 width from 3.5 mm to 1.0 mm produces a reduction in w_{cc} from 20 arc secs to 12 arc secs. An explanation for this phenomenon is given in Subsection 5.4.2. Further reduction of Slit 3 width to 0.5 mm produced no change in w_{cc} and so the 1.00 mm setting was employed for short wavelength (1,-1) rocking curves. At longer wavelengths larger Slit 3 settings were used since within certain experimentally determined limits this incurred no broadening of the rocking curve and allowed the beam divergence to be substantially greater than w_{cc} . The lattice tilts were aligned at 2.75 Å since at this wavelength w_{cc} smaller than at other emission line wavelengths used in the study.

A study of the main body and wings of each rocking curve was made as described in Section 3.4. Measured values of w_{cc} , $(\Delta\lambda/\lambda)_{cc}$, P_{cc} for perfect material are shown as filled circles on Figs.6.10, 6.12, 6.14 respectively. Measurement uncertainties on w_{cc} , $(\Delta\lambda/\lambda)_{cc}$ values are typically 3% and on P_{cc} values 1.5%. Fuller details are given in Tables 6.3, 6.4. Apart from at 5.73 Å the measured result is satisfyingly close to the Prins perfect lattice result. At present no thorough calculation of the Prins function taking into account resonance line excitations exists for the ADP(101) PK edge wavelength region and so it is difficult to make comment on the discrepancy between the measured and calculated results at 5.73 Å. Since, with the exception of the above discrepancy, the measured result is within less than 10% of the calculated result, an attempt to determine the line spread function by the fit procedure was in order. An effort was made to obtain a fit at 5.73 Å also, in spite of the doubt in the calculated result and the difference (~25%) between the measured and calculated result at this wavelength. A fit of the self-convolution of the Prins function to within a few percent of w_{cc} and P_{cc} of the (1,-1) rocking curve was obtained at all wavelengths. The parameters used to obtain a fit are listed in Table 6.5 and the widths of the major and minor Gaussian spread functions are plotted in Figs. 6.17, 6.18 respectively. At 9.52 Å a small absorption correction was used in the fit procedure in order to bring the calculated P_{cc} down to the measured value but at all other wavelengths only the two Gaussian spread functions were required. The fwhm of the major Gaussian spread function is everywhere small with respect to that of the Prins function thus showing that only a small perturbation of the latter function was required to obtain a fit. It should be noted that as observed for EDdT the widths of the major and minor Gaussian spread functions increase with increasing wavelength. An explanation of this feature is given in Subsection 5.4.2. It is noted that in accordance with the discussion given in Subsection 2.2.2, the minor Gaussian function makes a small contribution to the total spreading Figures 6.19.1a, 6.20.1a, ... 6.27.1a present for of the Prins function. each wavelength a linear plot of the fit to the (1,-1) rocking curve (continuous line) superimposed on the rocking curve (stepped line). Logarithmic plots of these curves are shown in Figs.6.19.1b,6.20,1b,... 6.27.1b with measured points obtained from the (1,-1) rocking curve wing studies shown as dots. Apart from at λ 7.13 Å where the fit P is about 6% lower than the measured $\ensuremath{\,P_{\rm cc}}$, the fit obtained is good to $\ 2$ or 3 orders of magnitude down on ${\rm P}_{\rm cc}$.

The parameters w, $(\Delta\lambda/\lambda)_{c}$, P of the line spread function derived from the fit are shown as filled circles on Figs.6.9,6.11,6.13 respectively. The fit result is everywhere close to the Prins result except for the anomalous discrepancy at 5.73 Å in the $w_{c}(\lambda)$ and $P_{c}(\lambda)$ results. The pattern of the fit and Prins result is thus very similar to that of the 2-reflection measured and calculated results. In view of this fact (and, related to this, the small perturbation required in the fit procedure) the fit function parameters can be regarded as being very close to those of the true line spread function. This conclusion is verified further in the plots of the fit and Prins perfect lattice functions for σ -, π - polarised and unpolarised radiation presented in Figs.6.19-6.27. In all cases the curve of lower peak value and with higher wings is the fit function. These plots show that the perturbation of the Prins function required in the fitting procedure is so small that in most cases the fit function still has a similar shape to the Prins function. It is therefore most probable that the fit functions obtained are a good representation of the perfect sample line spread function, at least in the main body of the function curves. In the far wings of the plots there is considerable discrepancy between the fit and Prins curves and therefore in these regions the fit curve can only be used as a guide as to the behaviour of line spread function.

<u>ii. Aged material</u>. A study of the effects of aging on the line spread function was made by measuring (1,-1) rocking curves using an aged sample (described in Subsection 6.4.1) as the test crystal and perfect sample as the monochromator. Measured values for w_{cc} , $(\Delta\lambda/\lambda)_{cc}$, P_{cc} are shown as open circles in Figs.6.10,6.12,6.14 respectively. In view of the small difference in $R_c(\lambda)$ with sample aging the change in the (1,-1) rocking curve parameters is surprisingly large. A possible explanation is that since the increase in $w_{cc}(\lambda)$ is but a small fraction of Prins perfect lattice $w_{c}(\lambda)$, the mosaic spread in the aged sample must be small so that secondary extinction is high. Also as commented upon in Subsection 6.4.1 the fact that the $R_{c}(\lambda)$ zero extinction limit is not far from the Prins perfect lattice limit does not allow much increase in $R_{c}(\lambda)$ for an enhancement in mosaic character.

iii. Sample spread of characteristics; flown samples It would appear from the above result that the sample spread in the $w_{cc}(\lambda), P_{cc}(\lambda)$ results is appreciably larger than that found in the $R_{cc}(\lambda)$ results. This was verified by the results for the Skylark 1206 and 804/1101 analysers shown as open triangles and open squares respectively on Figs. 6.10,6.12,6.14. These figures show that the results for the two rocket analysers are appreciably removed from each other and also from the perfect and aged sample results. It is therefore essential that a given sample should be calibrated before usage and thereafter checked periodically.

<u>iv. Processed material</u> In view of the fact that the aim of the SiC grit abrasion technique, namely to increase $R_c(\lambda)$, had not been achieved there was little value in studying the effect of the technique upon the (1,-1) rocking curve and so results are not included in Figs.6.10,6.12, 6.14. Nevertheless as a point of information the (1,-1) rocking curves observed were possessed of very high wings, whilst w_{cc} was up by an order of magnitude and P_{cc} down by a factor 30 on the perfect material result.

b. Discussion

The perfect material $w_{cc}(\lambda)$, $(\Delta\lambda/\lambda)_{cc}(\lambda)$, $P_{cc}(\lambda)$ results are everywhere close to the Prins result indicating not only the validity of calculating and measuring procedures but also the high surface quality produced through solution polishing. It is noteworthy that there is good agreement between the results presented here and those (where available) of other workers. Deslattes et al¹¹⁸ in a study of the perfection of solution grown, solution polished samples quotes for one crystal pair $(\Delta\lambda/\lambda)_{cc} = 1 \times 10^{-4}$ and $P_{cc} = 0.25$ at 8.34 Å. In the present study the values $(\Delta\lambda/\lambda)_{cc} = 1 \times 10^{-4}$ and $P_{cc} = 0.27$ at 8.34 Å were obtained.

The closeness of the measured results of the perfect material and the calculated results allowed the fit procedure to be executed within the limitations outlined in Subsection 2.2.2.d. i.e. only small perturbations to the Prins function were required. Consequently the shapes of the line spread functions obtained from the fit were still close to those of the original Prins function shapes. This suggests that the line spread functions obtained are very good approximations to the true line spread functions and one may conclude that in cases such as this one where perturbations to the Prins function are small the validity of the results of the fit procedure is high.

The observed broadening of the (1,-1) rocking curve due to sample aging should be considered in the light of the study made by Deslattes et al^{116,118} in which it was found that exposure of a pair of crystals with (101) surfaces to 50% relative humidity for about one month produced significant broadening in the 202 reflection (1,-1) rocking curve. However Burek et al¹⁰⁹ found that the reflectivities and widths of freshly solution polished samples were

stable for months, even when the samples were exposed to 100% relative humidity for a day and to accumulated irradiation to several days total exposure. It is difficult to make comparisons between the treatments applied by Deslattes and Burek but since the exposure times used in the latter treatment are relatively short it is most likely that this treatment is considerably less severe. Burek's findings suggest that provided ADP samples do not undergo severe attack then (1,-1) rocking curve parameters are stable for several months at least. This is borne out in the present study by the results for the Skylark 804/1101 sample. This sample had been exposed intermittently to the laboratory atmosphere during a period of at least 1 year and yet the increase in $w_{cc}(\lambda)$ is less than 10% above the perfect material result. The results for the aged material in the present study suggest that in time sample deterioration becomes very significant.

Line	λ (Å)	Perfect Direct Fit		Aged	Skyl Flight 1206	ark Samples 804/1101
Ti Kα K Kα Ru La S Kα Nb Lα P Kα Si Kα Al Kα Mg Kβ	2.75 3.74 4.85 5.37 5.73 6.16 7.13 8.34 9.52	$ \begin{array}{r} 10.9\\ 14.5\\ 21.5\\ 24.4\\ 28.6\\ 25.2\\ 37.8 \pm 1\%\\ 54.3 \pm 1\%\\ 87\\ + 3\% \end{array} $	10.84 14.39 21.67 24.30 28.59 25.28 37.76 53.87 87.02	15.2 ± 5% 27.9 31.8 63 + 3%	13.6 24.8 29.1 61 + 3%	12.0 58 + 3%

Table 6.3 ADP(101) Measured values of the 2-reflection fwhm w_{cc} (arc sec)

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	λ		Skvla	rk		
Line	(Å)	Direct Fit		Aged	Flight Samples 1206 804/1101	
Τί Κα Κ Κα	2.75 3.74	0.437	0.438	0.295	0.320	0.400
Ru La S Ka	4.85 5.37	0.256 0.209	0.250 0.207	0.160	0.182	
Nb La P Ka Si Ka	5.73 6.16 7.13	0.132 0.324 0.338	0.135	0.221	0.252	
Al Kα Mg Kβ	8.34 9.52	0.272 0.186 ± 4%	0.266	0.195	0.208	0.235
Ū		±1.5%		±1.5%	±1.5%	±1.5%

Table 6.4	ADP(101)	Measured v	alues o	of the	2-reflection	peak
		reflection	P			

λ (Å)	Absorption Correction	Major Gaussian fwhm (arc sec)	Minor Gaussian fwhm (arc sec)	Ratio 1	Ratio 2	w _c (arc sec)	Pc
2.75 3.74 4.85 5.37 5.73 6.16 7.13		1.125 1.00 2.25 2.00 3.75 2.50 4.50	25 45 70 70 70 80 130	0.92 0.94 0.97 0.96 0.93 0.96 0.97	0.08 0.06 0.03 0.04 0.07 0.04 0.03	7.47 9.53 13.2 14.3 16.8 15.6 24.6	0.700 0.580 0.374 0.287 0.172 0.389 0.272
8.34 9.52	0.1	5.00	190	0.97	0.03	50.9	0.264

Table 6.5 ADP(101) Fit parameters and characteristics of the fit line spread function





Figure 6.9 ADP(101) 1-reflection fwhm





Figure 6.11 ADP(101) 1-reflection resolution



2-reflection re





Figure 6.14 ADP(101) 2-reflection peak reflection


Figure 6.15 ADP(101) 1-reflection fwhm for reflection orders n = 1 - 4





Figure 6.17 ADP(101) fwhm of the major Gaussian used in the fit

R



Figure 6.18 ADP(101) fwhm of the minor Gaussian used in the fit



(a)

(c) $P_{\lambda}(\theta)$, unpolarised radiation, calculated Prins perfect lattice and fitted functions

(d) as (c) plotted with logarithmic ordinate

Figure 6.19.1 ADP(101) $P_{\lambda}(\beta)$, $P_{\lambda}(\theta)$ calculated and measured, unpolarised radiation, $\lambda 2.75$ NOTES ON THEORETICAL MODELLING GRAPHS AS FOR CHAPTER 5





 $P_{\lambda_{\Pi}}(\theta)$ Prins perfect lattice and fitted calculated functions (c)





15,00'00"

14 58'00"

10+

10-3

 π polarisation components, λ 2.75 and р $P_{\lambda}\left(\theta\right)$ Prins calculated and fitted, ADP(101) Figure 6.19.2



(a) $P_{\lambda}(\beta)\text{, unpolarised radiation, measured and fitted}$



(c) $P_{\lambda}\left(\theta\right)$, unpolarised radiation, calculated Prins perfect lattice and fitted functions





 $P_{\lambda}\left(\beta\right),P_{\lambda}\left(\theta\right)$ calculated and measured, unpolarised radiation, $\lambda\;3.74$ Figure 6.20.1 ADP(101)







as (c) plotted with logarithmic ordinate

(p)

20°37'00"

20,35,00,

20°33'00'

20°35'20"

20°35′00"

20°34'40'

0.0

0.2

7·0

104

103

10'























 $P_\lambda(\theta)$, unpolarised radiation, calculated Prins perfect lattice and fitted functions

(c)

plotted with logarithmic ordinate

(c)

as

(p)

λ 5.37 $P_{\lambda}(\beta)$, $P_{\lambda}(\theta)$ calculated and measured, unpolarised radiation, ADP(101) Figure 6.22.1















(a) $P_{\lambda}(\beta)\,\text{, unpolarised radiation, measured and fitted}$



(c) $P_\lambda(\theta)$, unpolarised radiation, calculated Prins perfect lattice and fitted functions







 $P_{\lambda}(\beta)$, $P_{\lambda}(\theta)$ calculated and measured, unpolarised radiation, λ 6.16 Figure 6.24.1 ADP(101)

















51°38'30"

51°36'30"

0.0

0.2

as (c) plotted with logarithmic ordinate

(p)

51°40'00'

51°30′00″

10

10-3





(a)



(c)





63°30′00″

63°28'00″

-0·0

0.1

-E-O

0.2

(c) plotted with logarithmic ordinate

as

(p)

63 40'00"

63°30'00'

63 20'00"

10,4

10-3

10⁻²







(c) $P_{\lambda\pi}(\theta)$ Prins perfect lattice and fitted calculated functions







polarisation components, A 9.52 Ħ and σ $\mathbb{P}_{\lambda}(\boldsymbol{\theta})$ Prins calculated and fitted, ADP(101) Figure 6.27.2

CHAPTER 7

BRAGG REFLECTION CALCULATIONS FOR SORBITOL HEXA-ACETATE (110)

7.1 Introduction

The confidence gained in the calculated results in previous crystal studies is an incentive to calculate the Bragg reflection characteristics of the rather interesting analyser sorbital hexaacetate for which only scanty measured data is available. Interest in sorbitol hexa-acetate (SHA, $C_6H_8O_6$ (COCH₃)₆, 2d = 13.88Å) as a Bragg analyser was aroused in the early 1960s by Gavrilova's report, that for Cu Ka radiation the reflection efficiency^{\dagger} of SHA is up by a This result was confirmed by Ruderman and Michelman $^{126}\,$ factor 3 on PET. and also by Leigh⁸¹, the latter finding SHA to be up by a factor 2 on PET. These findings must however be treated with caution since without further information from calculations and experimental studies interpretation is difficult. This matter is addressed further in Section 7.3. SHA is a potentially useful crystal for X-ray fluorescence analysis in the 9-14Å wavelength range. Currently used analysers suffer from the disadvantages of either exhibiting crystal fluorescence (e.g. ADP) or low angular dispersion due to a large 2d (e.g. phthalates, stearates). SHA provides sufficient angular dispersion in the above wavelength region and X-ray fluorescence studies at Mg K α have shown that, as a result of containing only low Z elements, background contamination in the Mg Ka region due to crystal fluorescence is negligible. Indeed, although SHA has a lower reflection efficiency than ADP (by factor 2) the problem

⁺The expression reflection efficiency is commonly found in X-ray spectrometry nomenclature. It is dependent upon the geometric conditions under which the crystal is used as well as the reflection integral (see Ref.128).

of variable background contamination due to $P \ K \alpha$ fluorescence radiation when using ADP, favours the use of SHA for routine measurement of Mg K α radiation. In the case of the measurement of Na K α there is little possibility that SHA will supercede RAP since the contamination free background could not compensate for the very high reflection efficiency losses.

Extensive use of SHA is hampered by the difficulties encountered in the production of high quality samples. 127,128,129 In particular, temperature variations during growth cause thermal stresses in the crystal which lead to cracking. Crystal samples also tend to exhibit twinning. However in the last decade significant improvements have been made in sample preparation and it is possible, in principle at least, to produce SHA commercially. With this and the potential usefulness of the crystal in mind it is worth studying this analyser albeit The following calculations augment the mostly by calculation. reflection integral measurements of Leigh on a single crystal of SHA which showed appreciable thermal cracking. Expense prevented the procurement of two samples and hence rocking curve studies were not made. In any case it is worth waiting until high quality samples are available before carrying out such a study.

7.2 Data Sources and Details of Numerical Evaluation

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The crystal structure of SHA was determined by Dr. D.R. Russell¹³⁰ of the Chemistry Department of Leicester University using a sample supplied by Isomet Corporation[†]. This structure determination also

Isomet Corporation, 433 Commercial Avenue, Palisades Park, New Jersey, 07650, USA.

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provided anisotropic temperature parameters for oxygen atoms and isotropic temperature parameters for carbon and hydrogen atoms and these were used in the calculations to follow. The crystal density was obtained from Ref.129. Since the constituent atoms of SHA have low Z numbers and the reflection wavelength range is well removed from the absorption edges of those atoms, it was appropriate to use Hönl's method to calculate anomalous dispersion terms.

7.3 Comment on the Calculated Results

At present the lack of measured values of the linear expansion coefficient α does not allow an evaluation of the Bragg dispersion function. However, in anticipation of this datum becoming available, the calculated function $\Delta\theta(\lambda)$ is shown in Fig.7.1 and literature values of d are given as follows:

$$d_{23} = 6.995 \pm 0.005 \text{ Å}^{127}$$

 $d_{20} = 6.941 \pm 0.007 \text{ Å}^{130}$

The calculated $R_c(\lambda)$ results are shown in Figure 7.2. Also included are the measured values of Leigh for a single crystal of SHA supplied by Isomet Corporation. The calculated results show the commonly observed large separation between the Prins and Darwin zeroextinction results at short wavelengths. A comparison of the calculated and measured results at short wavelengths shows that the crystal sample has considerable mosaic character. In view of the thermal cracking in the sample this is not surprising. In order to interpret the aforementioned SHA and PET results of Gavrilova and others it is instructive to compare Figure 7.2 with Figure 4.3 which summarises calculated and measured R_c data for PET. Clearly at 1.54 Å the calculated R_c of PET is higher at the Prins perfect lattice limit and particularly so at the zero-extinction limit. This suggests that the measured result for SHA appears higher only because a mosaic SHA is being compared with a perfect PET. If the SHA and PET samples were of comparable quality then undoubtedly PET would show a higher reflection efficiency.

Figure 7.2 also shows a depression in the SHA Prins, zeroextinction and measured $R_c(\lambda)$ results in the 9.5 Å region. In view of Darwin zero-absorption result at 9.5 Å this suggests a high unit cell absorption cross section. Clearly this is a disadvantage for X-ray fluorescence analysis of Mg containing materials previously discussed in Section 7.1. The small separation of the Prins and zero-extinction results in this wavelength region shows that there is little to be gained in R_c from surface abrasion processes.

The calculated $k(\theta_{\rm E})$ results shown in Figure 7.5 are remarkable by virtue of the low Prins result for $\theta > 45^{\circ}$. Indeed the Prins result is very close to the zero-extinction limit. SHA is therefore a potentially useful crystal in polarimetry experiments where analysers possessed of a low $k(\theta_{\rm B})$ characteristic are required.

A plot of $R_c^n(\lambda)$ for reflection orders 1-4 as shown in Figure 7.6 demonstrates that second order $R_c(\lambda)$ is non-negligible and that care must be taken in first order measurements to ensure that second order contamination is eliminated or taken into account.

Figures 7.7 - 7.14 present calculated results which relate to the width and peak of the line spread function. For the reader interested in the application of SHA to spectroscopic studies, the $(\Delta\lambda/\lambda)_{\rm c}(\lambda)$ plot given in Figure 7.9 is of most interest. A typical value $(\Delta\lambda/\lambda)_{\rm c} = 1.15 \times 10^{-4}$ means that the resolving power of SHA is comparable with that of ADP for which $(\Delta\lambda/\lambda)_{c} = 1.2 \times 10^{-4}$. Provided high quality samples can be produced commercially, SHA clearly shows promise for use in X-ray spectroscopy.

7.4 Conclusions

The above calculations show that outside the 2d limit wavelength regions, SHA is comparable to ADP with respect to $R_{c}(\lambda)$ and $(\Delta\lambda/\lambda)$ (λ) results. A comparison of both measured and calculated results for SHA and PET indicate that SHA has the lower $R_{c}(\lambda)$ and that measured results to the contrary at 2.75 Å are deceptive because a mosaic SHA sample result is being compared with a perfect PET sample The calculations also show that SHA has an appreciable result. second order $R_{\rm C}(\lambda)$ and that care will be needed in avoiding second order contamination in first order measurements. SHA is potentially useful in X-ray fluorescence analysis particularly for Mg K α radiation where on account of low background contamination due to crystal fluorescence it provides a useful alternative to ADP. Unfortunately it is not possible to achieve the reflection efficiency of ADP at Mg K $\!\alpha$. On account of a low $k(\theta_{B})$ characteristic at $\theta > 45^{\circ}$ SHA shows promise Furthermore by virtue of high potential as a polarimetry analyser. resolving power SHA may well find application in X-ray spectroscopy. It can be concluded from the above summary that SHA could be made use of in X-ray astronomy, although in large area crystal experiments the difficulty of growing crystals free of thermal stressing and twinning may be inhibitive. It is to be hoped that in the not too distant future high quality SHA samples will be commercially available.





Figure 7.2 SHA(110) Bragg reflection integral











Figure 7.6 SHA(110) Bragg reflection integral for reflection orders n = 1 - 4



Figure 7.7 SHA(110) 1-reflection fwhm



Figure 7.8 SHA(110) 2-reflection fwhm












Figure 7.13 SHA(110) 1-reflection fwhm for reflection orders n = 1 - 4



CHAPTER 8

CALIBRATION DATA FOR THE ARIEL 5 BRAGG SPECTROMETER

The main thrust of this thesis has been the application of calculation and measurement techniques to the thorough characterisation of particular Bragg analysers. The reliability of these techniques borne out by good agreement between theoretical and measured results and the high efficiency with which they can be applied has indeed led to their application to routine, but nevertheless important, calibration of analysers used in other research work. In this chapter a report is given of the calibration of graphite (002) and lithium fluoride (200) used in the Ariel 5 Bragg spectrometer and in Chapter 9 a report of the calibration of ADP (101), gypsum (020), KAP (001) and RbAP (001) for use in the American Science and Engineering (AS&E) rocket studies of the solar corona. Both reports are presented in their original form. Other work carried out but not given here include the calibration of PET (002) for use in X-ray analysis studies at Pye Unicam, Cambridge, and the calibration of various analysers for use in X-ray diagnostic experiments at the Rutherford Central Laser Facility.

CALIBRATION DATA FOR THE ARIEL 5 BRAGG SPECTROMETER

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Abstract. The principal characteristics of the Ariel 5 Bragg spectrometers are reported. In particular the preparation and calibration of the crystals are discussed and the calibrations presented.

1. Introduction

The Ariel 5 X-ray astronomy spacecraft (previously known as UK-5) carries a pair of conventional coarsely collimated flat crystal spectrometers for study of the spectra of night sky X-ray bright objects. Since launch (on 15 October, 1974) and to the time of writing the instruments have operated correctly in all respects; the scan mechanisms, control and data electronics are all functioning correctly and the gas proportional counters have shown stable performance and low background noise rate.

To the time of writing, observations on which the instrument has received substantial exposure include a thorough search of the SCO X-1 spectrum from the Fe xxv1 Lyman line to the K-shell ionisation limit. The spectra of both CAS A and the Tycho SNR have been examined for the presence of Si x1v Lyman α and the Fe xxv resonance line. A polarisation study of the Crab continuum spectrum has also been made.

All these results will be discussed elsewhere. Our present purpose is restricted to establishing the instrument calibrations upon which the interpretation of these data depend. The salient features of the instrument design are given in Table I. The (wavelength-dependent) detector quantum efficiencies may trivially be calculated

TABLE I

The salient design features of the Ariel 5 spectrometers						
Analyser type:		Graphite 002	Lithium fluoride 200			
Aperture:		221 cm ²				
Collimation:		Hexagonal honeycomb, FWHM≈7°				
Scan limits: Detectors:	θ (°)	31.8-69.6	23.3-61.6			
	λ (Å)	3.5- 6.3	1.6- 3.5			
	E (keV)	3.5- 1.9	7.7- 3.5			
	window	0.0034" Be	0.005" Be			
	gas mix	75% argon, 15% xenon,				
	C	10% methane				
	fill pressure	900 mms mercury				
	gas depth	2 cm				

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from the data given in the table using well-established mass absorption coefficients, for example those of Stainer [1]. In the remainder of this paper we are concerned with the more difficult matter of the calibration of the efficiency of the Bragg analyser crystals.

2. Definitions

If the direction of the maximum collimator transmission is directed to an X-ray star then the beam incident on the crystal is sensibly parallel and the glancing incident angle to the crystal is θ . If the source emitted a single monochromatic wavelength, λ , arriving at the spectrometer at unit power cm⁻², then the power diffracted from the crystal into the detector is $P_{\lambda}(\theta)$, and $P_{\lambda}(\theta)$ is sharply peaked about the value of θ which satisfies the Bragg condition

$\lambda = (2d/n)\sin\theta$

d is the period of the crystal lattice and n is the order of diffraction. We have discussed elsewhere [2] the difficulties of using calibrations of the fractional reflection $P_{\lambda}(\theta)$. However, if the crystal is rotated at constant speed ω through the region of significant Bragg reflection, then the total energy received by the detector, if the (monochromatic) input beam power is I_{0} , is

$$E = I_0 \int P_{\lambda}(\theta) \, \mathrm{d}\theta/\omega = I_0 R_c/\omega, \tag{1}$$

where R_c is the reflection integral. In a search for emission lines the Ariel 5 spectrometers are operated in a manner which implements Equation (1) and the required efficiency calibration is R_c .

In order to observe a continuum spectrum from the source it is sufficient, in order to measure the power $I_0(\lambda)$ at wavelength λ , to maintain θ constant and the power received by the detector is then [2]

$$J(\theta) = I_0(\lambda)\lambda R_c \cot \theta,$$

so that again the reflection integral is the required calibration.

3. Calibration of the Graphite Crystals

Since in X-ray astronomy the source power I_0 is always small, it is important to use the best available crystal efficiency. Lyttle and Bingham [3] pointed out the advantages of graphite from this point of view and Kestenbaum [4] made a study of the properties of commercially available graphite. Professor Novick's group have used the material for rocket- and satellite-borne spectrometers and have extensively reported their work [5].

The raw material procured for use in Ariel 5 was obtained from the same manufacturer as used by the Columbia group (Union Carbide Corporation) though

our preparation procedure was different (see Appendix) and the Bragg reflection characteristics were correspondingly different.

Figure 1 shows a summary of calculated and measured values for the reflection integral, as a function with wavelength, in which the Leicester and Columbia values are compared. The lower curves marked P are calculations for a perfectly regular graphite lattice according to the zero absorption Darwin limit, the upper curves marked M are for ideal mosaic crystal samples calculated according to the Darwin zero extinction limit. The Columbia results are plotted from the data in Reference [4]*. The Leicester calculations use mass absorption coefficients from Stainer [1], and our own calculations of the unit cell scattering factor. The latter is based upon the atomic coordinates given by Wyckoff [6] and the carbon scattering coefficients of Doyle and Turner [7]. The result of the calculation puts the unit cell structure factor F in the range 16.1 to 17.4 according to the uncertainty in Wyckoff's atomic coordinates. Professor Novick has pointed out to us the searching investigation of Ergun [8] which produces a similar value.

In Figure 1 the crosses are the Columbia measured values from Reference [4] and the single point at 4.75 Å for a similar sample prepared at Leicester is in quite good agreement – to about 15%. In fact there is no reason to expect better agreement than this because we have found that the amount of extinction in a thin graphite sample is dependent upon the method of sectioning, mounting, etc.

In the case of the Ariel 5 instrument there are several constraints on the scan limits which can be used in a given observation and these place an upper limit on the desired crystal diffraction width. The particular sample, of which one test result is shown by the open square at λ 4.75, was prepared in order to try to reproduce the maximised Columbia R_c values. The full width at half maximum (FWHM) of $P_{\lambda}(\theta)$ for this sample, however, exceeded 1° and was substantially too wide for use on Ariel 5. We therefore evaluated an alternative sectioning and mounting technique to find a narrower mosaic spread. The techniques as finally adopted for the preparation of the flight crystals were as described in the Appendix. These methods produced a FWHM mosaic spread of about 20' (see below), which was suitable for use on Ariel 5. These circumstances forced us to accept the increased extinction that inevitably accompanied a reduction in the mosaic spread and the consequent reduction in the reflection integral. The final Ariel 5 calibrations, shown by the solid line of Figure 1, thus show a penalty of about factor 2 in efficiency compared with the measurements of Kestenbaum.

For crystal samples with such wide mosaic spreads as are relevant here, it is a simple matter to make usefully accurate measurements of the shape of the diffraction profile $P_{\lambda}(\theta)$ as well as of the integral R_c . Thus the dispersion in θ of the natural width

^{*} In the verbal presentation of this paper at the Symposium our slide of Figure 1 compared the Leicester calculations as shown here with Columbia calculations taken from Kestenbaum, Columbia Astrophysics Contribution No. 89 (February, 1973). Our calculations were at variance with these data, but the discrepancy was removed in the revision to the Columbia data (10 May 1973) given in Reference [4] of which we were then unaware.

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Fig. 1. Calculated and measured values for the Bragg reflection integral R_c of graphite cleavage planes in first order. The curves marked M are the calculated Darwin mosaic limit; the full line is the Columbia result (Ref. [4]), the broken line is our result. The curves marked P are the Darwin perfect lattice zero absorption limit; the broken line is the Leicester result and the dashed line is from Ref. [4]. The open square is an early Leicester measured value for comparison with the Columbia measured values given by the crosses. The solid line through the full circles is the final Ariel 5 calibration.



Fig. 2. The mosaic spread of graphite cleavage planes measured (in first order) with Ru L_{α} radiation at λ 4.85, (a) for an early Leicester sample, (b) for an Ariel 5 sample.

of fluorescent X-ray lines is generally less than 1 milliradian and it is easy to set slit widths to maintain the test beam parallel to about 1 milliradian also. Under these conditions a recording of the count rate (normalised to the count rate in the test beam), as θ is scanned through the reflection, is a good approximation to $P_{\lambda}(\theta)$. Figure 2a shows an example of such a record for the first high efficiency sample and Figure 2b shows a typical profile for the flight material.

Figure 3 shows the FWHM of $P_{\lambda}(\theta)$ plotted with wavelength. This shows our first test sample to have a somewhat larger spread than the Columbia material and the flight material to have a substantially smaller spread than either. All the experimental data show much larger diffraction widths than are predicted by the Darwin zero absorption perfect crystal model, results of which are shown for comparison.

Figure 4 shows the fractional peak value of $P_{\lambda}(\theta)$ graphed with wavelength. Note that, curiously, the Ariel 5 material does not show substantially higher fractional reflection than the Columbia material, despite the narrower profiles for $P_{\lambda}(\theta)$. It is doubtful whether these conclusions are much affected by differences in measurement conditions. The collimation used for the Columbia measurements was 0.19° and that used in the Ariel 5 calibrations was 0.15°. As Kestenbaum noted, this effect leads to underestimation of the peak fractional reflection and overestimation of the FWHM of $P_{\lambda}(\theta)$, but in both cases this is more like 10% than a factor of 2.

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Fig. 3. The full width at half maximum for first order graphite cleavage plane reflections graphed with wavelength. The lower curve is the calculated Darwin result for a perfect zero absorption lattice. The crosses are Columbia results from Ref. [4], the open square is a comparable Leicester result and the Ariel 5 calibrations are given by the solid line through the full circles.



Fig. 4. The fractional reflection at the peak of the diffraction profile for graphite. The Ariel 5 values are given by the solid line through the full circles. The open circles are Columbia results (Ref. [4]), the open square is a Leicester result for the early Leicester sample.

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Fig. 5. The reflection integral for first order LiF reflections. The faint curve is the calculated Darwin mosaic limit, the broken line is the calculated Darwin zero absorption perfect lattice limit and the solid line is the measured Ariel 5 calibration.

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Fig. 6. The measured (Ariel 5 sample) fractional reflection at the peak of the diffraction profile for first order LiF diffraction.

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4. Calibration of LiF Crystals

The lithium fluoride crystals used for the Ariel 5 high energy spectrometer were standard commercial grade material procured from Nuclear and Silica Products Ltd. The calibration procedures were as for the graphite considered above. Figure 5 shows the measured reflection integral R_c graphed with wavelength and compared with the calculated Darwin limits. Figure 6 shows the peak fractional reflection $P_{\lambda}(\theta)$ graphed with wavelength. In these data the systematic underestimation due to the effects of non-zero beam spread and bandwidth (see above) is more significant because the diffraction profiles are narrower. Figure 7 shows a (1, -1) two-reflection rocking curve at λ 3.45. The FWHM is 609".



Fig. 7. A two-reflection (1, -1) rocking curve for first order LiF in Ca Ka λ 3.45 radiation.

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Appendix

Preparation of the Graphite Crystal Panel for Ariel 5

Union Carbide grade ZYB graphite (mosaic spread $0.8^{\circ} \pm 0.2^{\circ}$ FWHM) was selected and procured in pieces 1 inch square by $\frac{3}{16}$ inch thick. Our initial experience with cleaving the graphite made it clear that cleaved crystal thicknesses of the order 0.01 inch were feasible as production items, providing that the thin crystal was fully supported during the cleaving operation. Ideally, cleavage should be initiated with a very thin blade: the strongly diverging blade of our Zeiss microtome was then unsuitable and was replaced by a commercial, single edged razor blade.

The production sequence was as follows:

(1) To each large face of a graphite slab a (1 square inch by 0.1 inch) magnesium alloy substrate was attached using epoxy cement. This sandwich was attached to the microtome carriage with a thermoplastic wax (commonly used to fix geological specimens during grinding, etc.).

(2) The blade on the microtome was used to initiate cleavage 0.01 inch from the upper substrate by attacking the graphite slightly towards one corner. The cleavage was then completed by hand and any stepping caused by torn layers was removed by peeling away the excess, from both faces, with tweezers.

(3) A new upper substrate was then attached with epoxy and the cleavage repeated until all the graphite was used.

(4) A crystal array sub-unit was formed of six of the 1 square inch crystals. These were waxed face down together onto an optical flat and then attached to a magnesium alloy sub-frame with enough epoxy cement to ensure that they stayed parallel.

(5) After removal of all the wax from the sub-unit, individual crystals were cleaned-up by removing thin layers of graphite from their surfaces with adhesive tape.

(6) Using the Leicester 80 foot X-ray facility, measurements were made on each sub-unit of

(a) the reflection integral R_c and the mosaic spread at a number of X-ray energies

(b) the angular relationship between the peak of the reflection and the lower face of the sub-unit.

Using specially machined shims a set of sub-units was then mounted, with crystals parallel, on a master frame.

CHAPTER 9

THE CALIBRATION OF BRAGG X-RAY ANALYSERS FOR USE IN AS & E ROCKET STUDIES OF THE SOLAR CORONA

The attached is a report of studies commissioned by American Science and Engineering Inc., 955 Massachusetts Avenue, Cambridge, Massachusetts 02139, U.S.A. The company had procured several large Bragg analyser crystals for use as the major optical elements in an instrument to be flown on high altitude rockets for the purpose of diagnosis of the condition of the sun's atmosphere. Extensive studies of the characteristics of these analysers were conducted by the present author and reported to the company. The methods used in the studies were as discussed in this thesis and details were made available to the company. Final results given to the company were as in the attached brief report which is reproduced here without further comment or modification (apart from updating the references) as one example of the contribution this present work has made to the work of others.

The Calibration of Bragg X-Ray Analyzers For Use In AS&E Rocket Studies of the Solar Corona.

Report of Measurements of the Efficiency and Resolution of ADP (1 sample), gypsum (2 samples), KAP (2 samples), RbAP (1 sample).

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 Wavelength Calibration. Although collimated Bragg spectrometers may be used to determine the coronal spectrum with a

wavelength precision of about 1 part in 20,000 we have previously argued¹. that it is generally preferable to establish this precision wavelength scale by selfcalibration of the recorded spectrum using carefully selected reference lines. However, as a protection against gross error, it is our normal practice to note the nominal Bragg angles at which each wavelength is reflected during the efficiency and resolution measurements given below. No particular care is taken to achieve precision in measurement of these angles(a zero error of up to 10 arc minutes could be present). However, it was noted that all reflections occurred at the expected angles within say ± 15 arc minutes. Angles were measured relative to the mechanical face of the crystals and S.Q & S nominal 2d values were used.

 Reflection Integrals.
 All samples were calibrated using the 2-reflection asymmetric method described by Evans et al².

The raw measured values are shown by individual points. In some cases a small calculated correction is applied to produce the final characteristic which is then shown as a solid line. Where two samples of a given material have been measured the second sample was studied at fewer wavelengths which were sufficient to show consistency. For comparison typical measurements on comparable Leicester material is shown as a faint line. The calculated predictions of the Darwin imperfect limit are also shown (as a broken line) for comparison.

3. Resolution. Though it is not entirely satisfactory it is world-wide practice at the present time to characterize the resolution of Bragg x-ray analyzers as the full width at half maximum (FWHM) of the 2-reflection (1, -1) symmettrical rocking curve as described in the standard texts (notably x-rays in Theory and Practice, A.H.Compton, S.K. Allison, Von Nostrand, New York 1935). The results are shown as a solid line through the measured values (no correction need be applied to the raw data in this case). Where two samples of the same material were tested no significant differences between the two were found. Except in the case of gypsum, typical previous

measurements on Leicester material are shown for comparison by flint lines. The broken curves represent the FWHM of the calculated zero absorption Darwin limit <u>single-reflection</u> curves.

In all the measurements the first crystal was a Leicester sample of comparable quality to the AS &E test sample (which was always mounted for the second reflection).

We considered that the quality of both gypsum crystals was worthy of special note. They are probably the best samples we have seen at Leicester.

References:

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	CALCULATED VALUES (DARWIN IMPERFECT LIMITFOR REFLECTION INTEGRAL, ZERO ABSORPTION LIMIT FOR RESOLUTION)			
	MEASURED VALUES (TYPICAL LEICESTER SAMPLES)			
Ŷ	MEASURED VALUES A.S. AND E SAMPLE 1 WITH CALCULATED POLARISATION CORRECTION.			
\$	AS ABOVE FOR A.S. AND E SAMPLE 2.			
	FINAL CALIBRATION FOR A.S. AND E SAMPLE 2			









CONCLUSIONS

The main purpose of this work has been the full characterisation of selected Bragg analysers both by measurement and calculation. This has involved applying efficient measurement techniques, some only developed in recent years, and taking advantage of available computational methods to calculate Bragg reflection characteristics based on models proposed early this century. In general where comparison between measurement and calculation is possible, e.g. between the results for fresh perfect crystal samples and the Prins perfect lattice model, agreement is, in general, remarkably close. This indicates the power of the Bragg reflection models and the validity of the measurement techniques applied.

The Bragg dispersion function study for PET showed that within the limits of measurement uncertainties the measured $\Delta\theta(\lambda)$ result agree with the well-attested calculated results. The main problem of the study was temperature control and measurement so that for future studies significant improvements are required in this area.

The effects of crystal aging upon Bragg reflection characteristics have been clearly demonstrated, and particularly so in the case of PET for which increases in the $R_c(\lambda)$ characteristic are very significant. This result is to be expected for PET on account of its softness and high water solubility and hence its high susceptibility to attack from the laboratory atmosphere. The calculated results for the Darwin zero-extinction limit indicate that it is possible to increase $R_c(\lambda)$ of a given sample above the measured aged sample results. Various treatments were applied to samples in an attempt to accelerate the aging process which in effect meant an increase in the mosaicity of the samples. The manufacturer's (Quartz et Silice) solution etching treatment, which was applied to PET

samples, produced a considerable increase in $R_c(\lambda)$. The SiC abrasion technique brought about an even larger increase for PET and was applied with success to EDdT samples also. Unfortunately the $R_c(\lambda)$ result for ADP was not improved significantly by the abrasion technique and indeed the calculated results show that, due to the relatively small difference between the Prins perfect lattice and zeroextinction limits, there is little room for improvement in any case.

One of the surprises of this study was the structure found in the PK absorption edge of ADP. This was later accounted for on the basis of resonance line scattering. Similar but even more severe structure has been observed in the OK edge of KAP in this and other An analysis of the PK edge is in progress at present. laboratories. The lesson to be learned from these observations of such structure is that presently available anomalous dispersion term calculations are sufficiently powerful outside an absorption edge wavelength region as is clearly demonstrated by good agreement between measurement and calculation, whereas within such a wavelength region these calculations are in general inadequate so that calculated results must be regarded with caution and should be supported by measurement. With regard to future work, the Bragg reflection technique shows great promise as a means of testing, and thereby modifying, theoretical descriptions of absorption edges.

Two important practical matters were highlighted in the (1,-1) rocking curve studies. In order to obtain undistorted curves, crystal mounting must be as stress-free as possible. The presence of macroscopic defects (such as bending strain) in crystal samples is very common and in consequence rocking curve widths are sensitive to the magnitude of the irradiated crystal surface area. This was clearly

illustrated by the excessively broad rocking curves obtained at low glancing angles for which (for fixed slit width settings) reflecting areas are large. The closest agreement between measured and calculated (1,-1) rocking curve characteristics was found for ADP . Indeed differences between measured and calculated w results for this analyser were less than 10%, thus showing the high sample quality resulting from both crystal growth and solution polishing. A lesser degree of agreement was found for EDdT and PET although in the latter case this was to some extent due to the fact that the crystal surface reflecting areas were large. These results seem reasonable in view of the fact that the softer organic materials are more susceptible to chemical attack and mechanical stress. Increases in w_{cc} due to sample aging were found to be commensurate with increases in R_{c} due to the fact that reduction in the extinction limitation on R_c results from spreading of the orientation distribution of the crystal domains. Accordingly sample aging produced large changes in both w_{cc} and R_{c} . for PET and small changes in both these characteristics for EDdT. This study has gone some way towards clarifying the effects of aging upon ADP which has been under debate due to seemingly contrary observations. It would appear from the present (1,-1) rocking curve studies that ADP ages slowly but in time (5 years or so) will degenerate appreciably. It was found that several of the surface treatments applied to increase reflection efficiency (e.g. sand blasting and steam blasting) produced mis-shapen rocking curves often with excessively high On the other hand the solution etching and SiC grit abrasion wings. techniques produced well-formed rocking curves. It should be noted that only relatively few techniques were tried since essentially the aim was to show that reflection efficiency could be significantly improved.

There is room for considerably more experimentation in this area particularly in say the application of any one technique in varying degrees.

This study has presented a method for obtaining the line spread function of a crystal sample by means of fitting the self-convolution of the Prins function to the (1,-1) rocking curve. Perturbations to the Prins function were such as modelled the effects of lattice defects. The method as far as it has been developed was applied with greatest success to the ADP samples used in this work. This is due to the fact that since measured and calculated results for this analyser are close, in order to obtain a fit the required perturbations to the Prins function were small and therefore the conditions upon which the fit procedure is based were met. As a result the fit line spread functions for ADP were still possessed of the characteristic asymmetric shape of the present Prins functions. In the case of PET larger perturbations of the Prins function were required but these were still sufficiently small to give satisfactory results at all but the shortest At these wavelengths the fit procedure in its present wavelengths. state was not able to accommodate the macroscopic defects accentuated at Clearly a useful future exercise would be to low glancing angles. develop the procedure further such that these defects can be successfully modelled. In the EDdT study significant discrepancy between measured and calculated results was found so that appreciable perturbations of the parent Prins functions were required and accordingly there is less confidence in the results of the fit. This highlights the fact that at present the fit procedure is only applicable when there is good agreement between measurement and calculation. Since for many crystal samples such agreement is not found it is worth investigating methods for modelling lattice defects which have a severe effect upon crystal line

spread functions. In conjunction with this a useful future study would be a test of the fit procedure involving comparison of the fit and measured line spread functions, the latter being determined possibly by one of the methods discussed in Subsection 2.2.2. The problem of low count rates associated with these methods could be overcome by the use of powerful synchrotron X-ray sources.

APPENDIX A

COMPUTER PROGRAMS

Over the last few years several computer programs, which execute Bragg reflection calculations, have been written at Leicester for the following reasons. Calculation of Bragg reflection characteristics as predicted by the models discussed in Chapter 1 allows, through comparison of measured and calculated results, comment on the quality of the sample under study. The calculated results indicate the salient features in characteristic vs. λ results and so are of assistance in planning an experimental study of a particular analyser e.g. in the choice of emission line wavelengths at which measurements are made. The fit procedure (see Subsection 2.2.2.d) used to determine the crystal line spread function is clearly dependent upon computational techniques. The 1-reflection absorption edge studies (see Subsection 3.4.4) requires programs to analyse the 1-reflection scans and thence to relate the observed and theoretically predicted edge structure. 63,122 The various programs written, resulting from the above motivation, have been collected together to form a suite of programs which have identical data input formats and share a common library of subroutines.

The general organisation of individual programs may be appreciated with the aid of Fig.A.1. For the sake of clarity and brevity many calculation stages, particularly those common to two or more programs, are stored in the library of subroutines. The latter

¹ The development of the computer programs has required the assistance of several workers, a list of whom is given in the author's acknowledgements.

includes three subroutines for calculating atomic scattering factors, distinguished by the use of the Hönl, Parratt and Hempstead, and Cromer and Liberman methods for calculating the anomalous dispersion terms.[†] Also included are three subroutines for evaluating the geometric structure factor for a given atomic species using Debye-Waller, isotropic and anisotropic temperature parameters.

Input data for each program is divided into two blocks:

- a. Crystallographic data this is the data given by crystal structure analysis e.g. lattice parameters, atomic co-ordinates, temperature parameters, crystal density etc.
- b. Atomic data required for the calculation of atomic scattering factors. This data includes parameters relevant to the method chosen for the calculation of anomalous dispersion terms.

The data is fed on to two separate tapes designated by the main program. The latter also designates the subroutine for calculating geometric structure factors and hence from above the temperature parameters. The subroutine for calculating atomic scattering factors is also selected. Attached to each program is a common crystallographic data input routine called subroutine CRYSTAL. This subroutine reads the crystallographic data from tape and calculates the geometric structure factor for a given atomic species using the selected temperature parameter subroutine. The main program then goes into a wavelength loop within which the selected subroutine for calculating atomic scattering factors is called,

Common to each of these subroutines is the evaluation of f using the analytical expression given in Ref.32.

+

the main calculations of the program are executed and the data is outputted.

General outlines of the programs relevant to the present work are given on the following pages. In order to avoid repetition of details given above, only step d. of Fig.A.1 is covered in the outlines.

Program			а. b.	Designate i.tapes for crystallographic, atomic and output data ii.temperature parameters iii.method for calculating anomalous dispersion terms Call subroutine CRYSTAL - see below
	λ	- 100p	c. d. e.	Call subroutine which reads atomic data and calculates atomic scattering factors using designated method for anomalous dispersion terms Execute required calculations using the subroutine library and data from subroutine CRYSTAL Output data
Subroutine CRYSTAL			а. b. c.	Read crystallographic data Call subroutine for calculating geometric structure factors using selected temperature parameters Output geometric structure factors for atomic species

Library of subroutines



DARWIN PROGRAM

```
This program computes the Darwin zero-absorption function
P(\varepsilon) and its integral from analytical expressions.
                                                                     There is a choice
of numerical or analytical calculation of the 2-crystal function P(\beta).
Full details of this program are given in Ref.63. Subscripts \sigma, \pi
and u refer to the \sigma-, \pi-polarised and unpolarised cases respectively.
          Calculate the structure factors (excludes anomalous dispersion
          terms) and parameters for \sigma and \pi polarisations
          Adjust step length to give odd number of points in tail and
          flat regions of function
          Calculate P_{\sigma}(\varepsilon) and P_{\pi}(\varepsilon) analytically
          Calculate P_{u}(\varepsilon) by averaging P_{\sigma}(\varepsilon) and P_{\pi}(\varepsilon)
          Determine w numerically
          Calculate w_{c,\sigma} and w_{c,\pi\downarrow} analytically
          Calculate R_{c,\sigma}, R_{c,\pi} and R_{c,u} analytically
Calculate P_{\sigma}(\beta) and P_{\pi}(\beta) numerically Calculate P_{\sigma}(\beta) and P_{\pi}(\beta) analytically
Calculate P_{u}(\beta) from P_{\sigma}(\beta) and P_{\pi}(\beta) Calculate P_{u}(\beta) from P_{\sigma}(\beta) and P_{\pi}(\beta)
Determine w_{cc,\sigma}, w_{cc,\pi} and w_{cc,u} numerically Calculate w_{cc,\sigma} and w_{cc,\pi} analytically
                                                    Determine w_{cc,u} numerically
                    Calculate R_{cc} analytically
```

PRINS PROGRAM

This program computes the Prins perfect lattice limit crystal response function $P(\ell)$ and calculates its characteristics numerically. The function is convolved numerically to generate the 2-crystal response function $P(\beta)$ and the characteristics of this function are calculated numerically. Full details of this program are given in Ref.131.

> Calculate the refractive index terms δ_i and β_i Calculate the Prins D and B factors and total values for δ and β Calculate the deviation from the Bragg angle and the effective 2d -spacing Calculate $P_{\sigma}(l)$ and $P_{\pi}(l)$ Calculate $P_{\mu}(l)$ by averaging $P_{\sigma}(l)$ and $P_{\pi}(l)$ Calculate $R_{c,\sigma}, R_{c,\pi}$ and $R_{c,u}$ numerically using Simpson's rule Determine $w_{c,\sigma}, w_{c,\pi}$ and $w_{l,c,u}$ numerically Generate P (β) and P (β) by numerical convolution of single crystal response functions Calculate $P_{\mu}(\beta)$ by averaging $P_{\sigma}(\beta)$ and $P_{\pi}(\beta)$ Calculate R_{cc} values and w_{cc} values numerically Calculate the Prins polarisation factor k and the ratio R cc,u/R c,u Calculate centre of P_u(\dot{k}) by locating point at which area of curve up to this point is half the total area. Calculate deviation from Bragg angle and the effective 2d - spacing for this angle Graphical output of 1- and 2-crystal response functions
EWALD PROGRAM

This program calculates analytically 1- and 2-reflection crystal characteristics for the Darwin zero-extinction, Darwin zero-absorption and Prins perfect lattice models. Full details of this program are given in Ref.63.

> Calculate structure factor (excludes anomalous dispersion terms for Darwin zero-absorption model) Calculate linear absorption coefficient from anomalous dispersion terms Calculate R $_{c,\sigma}, R_{c,\pi}$ and R $_{c,\sigma}$ for the three models and w $_{c,\sigma}, w_{c,\pi}$ for Darwin Zero-absorption limit Calculate R $_{c,\pi}$ for the three models and w $_{c,\pi}$ for the three models and w $_{c,\pi}$ for the Darwin zero-absorption limit Calculate polarisation ratios for the Darwin zeroextinction and zero-absorption limits Calculate the deviation from the Bragg angle and the effective 2d-spacing

FIT PROGRAM

This program models defects found in real crystals in order to fit the self-convolution of the Prins perfect lattice function to the measured (1,-1) rocking curve. The graphical output of the perturbed Prins perfect lattice function describes the true line spread function of the measured crystal. The FIT program is essentially the PRINS program modified in the manner described in Subsection 2.2.2.d. i.e. the total value of β is multiplied by the factor 1 + x and the generated Prins function is numerically convolved with major and minor Gaussian spread functions. The fractional contribution of each of these two Gaussians to the spreading process is set by multiplying the amplitude of the Gaussian by the appropriate fraction. In order not to affect the integral of the parent Prins function the two fractions must add to unity.

<u>APPENDIX B</u> GEOMETRICAL DESCRIPTION OF THE 2-CRYSTAL SPECTROMETER WITH SPECIAL REFERENCE TO THE (1, -1) POSITION

Consider a 2-reflection system as described in Subsection 2.2.1. For an upolarised incident beam, which has a central ray of wavelength λ_0 making an angle θ_{m0} (the Bragg angle for λ_0)[†] with Crystal A surface, the general ray of this beam will be characterised by its wavelength λ , horizontal divergence α and vertical divergence ψ . The intensity of the beam reflected from Crystal B is given by the following expression

$$P_{ab}(\beta) = \frac{1}{2} \int_{\lambda_1}^{\lambda_2} \int_{-\alpha_m}^{\psi_m} \int_{-\alpha_m}^{\alpha_m} P_{a,m}^p (\varepsilon_a - z_m - \alpha) P_{b,n}^p (\beta - z_n \pm \alpha + \varepsilon_b)$$
(B.1)
× $G(\alpha, \psi) J(\lambda) d\alpha d\psi d\lambda$

where 1) Superscript 'p' refers to the polarisation component

- 2) Subscripts 'a' and 'b' refer to Crystals A and B.
- Subscripts 'm' and 'n' refer to the reflection orders of Crystals A and B
- 4) P_a and P_b are the respective line spread functions
- 5) The arguments of P_a and P_b are the differences between the glancing angle of the given ray and the appropriate Bragg angle θ_m or θ_n for that ray

6)
$$z_{\rm m} = \left(\frac{d\theta_{\rm m}}{d\lambda}\right)_{\lambda_{\rm o}} (\lambda - \lambda_{\rm o}) = \frac{\tan\theta_{\rm mo}}{\lambda_{\rm o}} (\lambda - \lambda_{\rm o})$$

- 7) β is the angle of rotation of Crystal B from a reference position at which the glancing angle for the general ray is $\theta_n - z_n \pm \alpha + \varepsilon_b$. β is positive in the direction of increasing glancing angle.
- 8) $\varepsilon_a(\psi, \delta_a)$ and $\varepsilon_b(\psi, \delta_a, \delta_b)$ the corrections to θ_m and θ_n due to vertical divergence and crystal tilt (δ) are given by the following expressions

$$\varepsilon_{a} = -\frac{1}{2}(\psi^{2} + \delta_{a}^{2})\tan n + \psi\delta_{a}/\cos n \qquad (B.2)$$

$$\varepsilon_{b\pm} = -\frac{1}{2}(\psi^{2} + \delta_{b}^{2})\tan \theta + [1/\cos\theta_{n}][\pm 2\delta_{a}^{2}\cos(\theta_{n}\pm\theta_{m})\sin\theta_{m}\pm 2\psi\delta_{a}\cos(\theta_{n}\pm\theta_{m}) - 2\delta_{a}\delta_{b}\sin\theta_{m} + \psi\delta_{b}] \qquad (B.3)$$

where $\eta = \theta_{m0} + \beta - \alpha$ and the upper and lower signs apply to the plus and minus positions respectively.

9) ψ_{m} and α_{m} are the maximum values of ψ and α respectively.

A geometrical proof of Expressions (B.1), (B.2) and (B.3) is given in

All Bragg angles mentioned in this discussion are corrected for the crystal refractive index.

standard texts. The nomenclature and conventions of Ref.65 have been adopted.

If the slits controlling the horizontal divergence of the beam incident upon Crystal A are sufficiently wide and the line spread functions are not excessively broad then, for a given wavelength, Bragg reflection will occur over a small range of α values. Now G(α, ψ) may be represented by the product

$$G(\alpha, \psi) = h(\alpha)g(\psi)$$
(B.4)

If $h(\alpha)$ is a slowly varying function (which is the case for wide slits and a narrow source) then the change in $h(\alpha)$ over the small range of significant α values can be neglected and so the incident beam intensity will be independent of α . Under these conditions Eqn. (B.4) can be written as

$$G(\alpha, \psi) = g(\psi) \tag{B.5}$$

The limits of the α -integration can also be extended to \pm^{∞} without affecting the value of the integral.

In the light of these points, and transforming variables such that

$$v = \varepsilon_a - z_m - \alpha$$
.Expression (B.1), for one polarisation component, becomes
 $P_{ab}(\beta) = \iiint_{-\infty}^{\infty} P_{a,m}(v) P_{b,n} \quad (\beta - z_n \neq z_m \neq v \pm \varepsilon_a + \varepsilon_b) g(\psi) J(\lambda) dv d\psi d\lambda$ (B.6)

where the limits of the ψ -and λ -integrals are as above.

For the (1, -1) parallel position the following simplifications may be made.

$$P_{a,m} = P_{b,n}$$
 Providing the crystals are identical
 $\theta_{no} = \theta_{mo}$ and therefore $z_n = z_m$

Expression (B.6) now becomes

$$P_{cc}(\beta) = \iiint_{-\infty}^{\infty} P(v)P(\beta + v - \varepsilon_a + \varepsilon_b)g(\psi)J(\lambda)dvd\psid\lambda$$
(B.7)

The arguments of the line spread functions are independent of z and therefore independent of λ and so the instrumental mode is non-dispersive. This property may also be derived from Eqn. (2.35). The functional forms of the line spread functions are slowly varying with wavelength and so the λ - integral may be separated out. It is shown in Subsection 2.3.1 that $g(\psi)$ gives rise to the geometrical window function $W(\beta)$ which convolves with the line spread functions to give the (1, -1) rocking curve. If the terms ε_a and ε_b are negligible, $W(\beta)$ has a very small width and so Expression (B.7) becomes

$$P_{cc}(\beta) = \int J(\lambda) d\lambda \int g(\psi) d\psi \int P(v)P(\beta + v) dv$$

= $S \int_{-\infty}^{\infty} P(v)P(\beta + v) dv$ (B.8)

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where S is a constant which is proportional to the intensity of the beam incident upon Crystal A. It is thus shown that for the (1, -1) position, under the conditions outlined above, (B.1) reduces to the relatively simple expression (B.8) which entails only the convolution of the line spread functions.

APPENDIX C

INVESTIGATION OF A PROPERTY OF CONVOLUTION INTEGRALS

Consider the convolution integral

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(\theta) P(\beta + \theta) d\theta d\beta$$
(C.1)

which appears in the numerator of Expression (2.48). This double integral can be simplified in the following manner. Replacing the variable β by a new

variable γ where

$$\gamma = \beta + \theta$$
; $d\gamma = d\beta$ (C.2)

Expression (C.1) becomes $\sum_{\infty}^{\infty} \sum_{\infty}^{\infty}$

$$\int_{-\infty}\int_{-\infty}^{\infty}P(\theta)P(\gamma)d\theta d\gamma$$
(C.3)

Taking the inner integral first, since this integration is with respect to $\ \theta$,

 $P(\gamma)$ may be regarded as a constant thus giving

$$P(\theta)P(\gamma)d\theta = P(\gamma) \int_{-\infty}^{\infty} P(\theta)d\theta \qquad (C.4)$$

Introducing the outer integral of (C.3) gives

$$\int_{-\infty}^{\infty} [P(\gamma) \int_{-\infty}^{\infty} P(\theta) d\theta] d\gamma$$
(C.5)
The term
$$\int_{-\infty}^{\infty} P(\theta) d\theta \text{ is a constant and thus (C.5) may be expressed as}$$
(C.6)

$$\left(\int_{-\infty}^{\infty} P(\theta) d\theta\right) \int_{-\infty}^{\infty} P(\gamma) d\gamma$$
 (C.6)

The limits of integration for each integral are the same and since γ differs from θ by a constant and not by a multiplication factor, the two integrals are equal. Therefore

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(\theta) P(\beta + \theta) d\theta d\beta = \left[\int_{-\infty}^{\infty} P(\theta) d\theta\right]^{2}$$
(C.7)

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ABSTRACT

A Quantitative Description of Bragg Analysers

Ray Hall

A detailed programme of methods for calculating and measuring crystal Bragg reflection characteristics is presented. The characterisation of an analyser involves determination of, as a function of wavelength, the Bragg dispersion function (defined in Chapter 2) and R_c , w, P, the integral, width and peak respectively of $P_1(\theta)$ the crystal line spread function (or diffraction profile). Calculations are based on the Prins perfect lattice, Darwin zero-extinction and zero-absorption models, outlines of which are given. Measurement methods for determining the Bragg dispersion function and P (θ) of an analyser are described. A comparison of various 1- and 2-reflection techniques used to measure $R_{c}(\lambda)$ is made and from this it is clear that the chosen 2reflection methods, with the inclusion of appropriate polarisation corrections, provide an efficient means of measuring this characteristic. Likewise a comparison is made of 1-, 2- and 3-reflection techniques previously used to determine $P_{\lambda}(\theta)$ and a new technique is introduced. This latter involves perturbing the calculated Prins function so that a fit between the self-convolution of the perturbed function and the (1, -1)rocking curve is obtained. Only perturbations which model the effects of known lattice defects are allowed. Within the limits discussed the perturbed function describes the true $P_{\lambda}(\theta)$. Emphasis is placed upon instrument alignment, and measurement conditions required, in all measurement techniques'used. A description of the Leicester 2-crystal spectrometer and its alignment is included, together with measurement procedures.

The above methods are applied in full characterisations of the analysers PET (002), EDdT (020) and ADP (101). Also included are calculated results for SHA (110) which allow interpretation of previous studies made by measurement alone. The thesis concludes with two brief reports of crystal calibration studies for the satellite UK5 and for American Science and Engineering. These reports illustrate the application of the methods used in this study to other research work.

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