VIBRATIONAL SPECTROSCOPY OF SOME

INORGANIC SINGLE CRYSTALS

A thesis presented for the degree of

Doctor of Philosophy

in the Faculty of Science

of the

University of Leicester

by

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University of Leicester

September, 1977

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Vernon H. Willings.

Statement

The accompanying thesis submitted for the degree of Ph.D. entitled "Vibrational Spectroscopy of Some Inorganic Single Crystals" is based on work conducted by the author in the Department of Chemistry of the University of Leicester, mainly during the period between October, 1974 and September, 1977.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references. None of the work has been submitted for another degree in this or any other University.

Hills

September, 1977.

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ABSTRACT

VIBRATIONAL SPECTROSCOPY OF SOME INORGANIC SINGLE CRYSTALS

This thesis contains the results of studies by single crystal vibrational spectroscopy of several materials. In an introduction the essential facts necessary for an understanding of the construction and nature of crystals in relation to single crystal vibrational spectroscopy are summarised. A review of i.r. reflectance spectroscopy is given as this was the major technique used in this research. A brief description of the Raman process is also given as well as methods of crystal growth used for this work.

Single crystal i.r. and Raman spectra for topaz are reported. A complete assignment is given for the v(Si-0) region; at lower frequencies there is a more or less continuous range of modes and any assignments in this region must be tentative. Some fragmentary data for spodumene are reported.

Single crystal i.r. and Raman spectra for AlCl₃.6H₂O are reported and, together with data collected from the deuteriate, enable an assignment to be given.

The assignment takes note of normal coordinate analysis calculations, deuteriation shifts, and factor group components, as well as solution data. An assignment for the modes due to water motions is given by comparison with previous assignments for mono- and di-aquated complex ions.

Far-i.r. spectra of HgCl₂ and HgBr₂ are reported at both ambient and low temperatures. For HgCl₂ the translatory modes have been identified from the fundamental modes predicted by theory, all of which have been observed. All the fundamental modes of HgBr₂ have been observed and assigned to symmetry species.

Far-i.r. spectra of three complex halides with the CsNiCl₃ structure are reported at ambient temperature. The results agree well with those reported previously for mulls and an unambiguous assignment is given.

Far-i.r. spectra of five square-planar complexes are reported at both ambient and low temperatures. Complete assignments for K_2PtBr_4 , $(NH_4)_2PtCl_4$ and $(NH_4)_2PdCl_4$ are given for the first time. In the case of K_2PtBr_4 v₄ and v₇ are accidentally almost degenerate at ambient temperature. The lattice mode region of the ammonium salts has been assigned; the breadth of the central region of i.r. mulls of these compounds is due to three bands occurring in close proximity. The occurrence of low temperature features in the chlorides has been confirmed, the possible origin of these modes is discussed.

A simplified factor group analysis scheme is given for the 80 diperiodic groups which lack periodicity in the third dimension. Examples of the use of the Tables are given.

Listings of computer programs used for i.r. reflectance analysis are given in the appendices.

This thesis is dedicated to my wife Linda,

and to my mother.

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Chapter One

The Theoretical Treatment of Crystals

•

Crystals and Symmetry

A crystal is a periodic three dimensional array of atoms, the smallest representative portion of which is called the "unit cell". The unit cell may be envisaged as a parallelepiped. By stacking a very large number of these unit cells along the three directions in a regular manner, the crystal may be constructed.

1.

Crystals are divided into seven crystal systems by the macroscopic symmetry which they possess. An explanation of symmetry will not be attempted here, but has been extensively reviewed by Cotton (1971). Figure 1.1 shows the essential symmetry axes of six of the seven systems. The seventh system, triclinic, is characterised by a total lack of symmetry axes. The essential symmetry axes represent the highest symmetry axes present and therefore define the system. Many other symmetry axes and elements are possible; the full cubic symmetry has thirteen symmetry axes and nine symmetry planes. The various combinations of symmetry elements in each system leads to a subdivision into thirty-two crystal classes. One class in each system will possess the full symmetry of the system and is called the holosymmetric class. Detailed accounts of the determination of crystal system by external morphology are given by Dana (1932); Cox, Price and Harte (1967), and Kirkaldy (1968). On a macroscopic scale it is sometimes difficult to distinguish orthorhombic crystals from those of the monoclinic system. In the absence of

Table 1.1

		Factor group symbols	
Crystal system	Unit cell constants	Schonflies	Herman-Mauguin
·			
Triclinic	αξβξγ	c ₁	1
	a t b t c	$C_i(S_2)$	ī
Monoclinic	$\alpha = \gamma = 90^{\circ} \beta \neq 90^{\circ}$	C ₂	2
	a t b t c	$c_{\mathbf{S}}(c_{1h})$	m
		C _{2h}	2/m
Orthorhombic	$\alpha = \beta = \gamma = 90^{\circ}$	$D_2(V)$	222
	a t b t c	C _{2v}	mm
		$D_{2h}(v_h)$	mmm
Tetragonal	$\alpha = \beta = \gamma = 90^{\circ}$	C4	4
	$a = b \neq c$	S ₄	4
		c _{4h}	4/m
		D ₄	422
		C ₄ v	4mm
		$D_{2d}(V_d)$	- 42m
		D_{4h}	4/mmm
Trigonal	$\alpha = \beta = \gamma \neq 90^{\circ}$	C ₃	3
(rhombohedral)	a = b = c	S ₆	3
		D ₃	32
		C _{3v}	Зm
		D _{3d}	- 3m

contd...

Hexagonal	$\alpha = \beta = 90^{\circ}, \gamma = 120$	C ₆	6
	a = b = c	C _{3h}	6
		C _{6h}	6/m
		D ₆	622
		C _{6v}	6mm
		D _{3h}	ēm2
		D _{6h}	6/mmm
Cubic	$\alpha = \beta = \gamma = 90^{\circ}$	Т	23
	a = b = c	Th	2/m3
		0	432
·		Td	4 3m
		Oh	4/m32/m

. .

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Figure 1.1

The essential symmetry axes of six of the seven crystal systems.



FIG.1.1



Orthorhombic



1

sufficiently developed faces, or in the case of a very small crystal, the system may be determined by the use of reflection goniometry, an account of which will not be attempted here. The "Barker Index of Crystals" lists common forms of many crystals. An analysis of interfacial angles with the optical goniometer may enable identification of the crystal to be made.

If the external form of a crystal can be said to possess symmetry, but is itself composed of a large number of unit cells, these unit cells must also possess the essential symmetry axes of the crystals.

Six parameters describe a parallelepiped. These are three angles α , β and γ and three lengths a, b and c. Figure 1.2 shows the relation of these parameters to the parallelepiped (which is the unit cell). The variation of these six parameters to create essential symmetry axes in the unit cell leads directly to the microscopic criteria which define the crystal system. The data are summarised in Table 1.1. The graduation from triclinic to cubic symmetry describes an ascent in symmetry.

In the crystal, the sides of the unit cell, and the angles between them, determine the stacking directions for the unit cells. The dimensions a, b and c now describe "crystallographic axes" of the crystal. It is obvious from Table 1.1 that cubic, tetragonal and orthorhombic systems have orthogonal axes. Monoclinic crystals have two orthogonal axes, 4.

FIG. 1.2



FIG. 1.3

monoclinic



β **ξ 90°**

triclinic



 $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$

the third axis is inclined towards one of these (see figure 1.3). In this system the b (or y) axis is sometimes referred to as the "unique axis" and corresponds to the diad axis of symmetry. Triclinic crystals have no specific relation between axes other than that all three angles are different and all three axes have different repeat lengths.

For convenience, in trigonal and hexagonal systems a fourth axis is introduced. The crystallographic c axis contains the three or six fold axis of symmetry. Perpendicular to c are three axes spaced at 120° to each other, all of equal length and in the same plane.

A knowledge of the relationship of the crystallographic axes to the external morphology is essential to a single crystal vibrational study. A crystal may be oriented in such a way that the crystallographic axes are either parallel or perpendicular to the polarisation of incident radiation. This enables information unique to certain directions within the unit cell to be obtained; a fuller account is given in Chapter Two.

Symmetry and the Unit Cell

A collection of symmetry elements, each of which corresponds to a symmetry operation, is called a group. The theory of groups is covered extensively by Cotton (1971) and Bradley and Cracknell (1972), the concepts introduced here are given in outline only.

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A symmetry operation may be expressed as a change of Cartesian coordinates from x_1 to x_2 ; y_1 to y_2 ; z_1 to z_2 . A change in coordinates for x_1 to x_2 may be expressed as:

$$\underline{\mathbf{x}}_2 = \underline{\mathbf{R}}\underline{\mathbf{x}}_1 + \underline{\mathbf{t}}$$

<u> Rx_1 </u> represents a rotation of the coordinate system around the origin, and <u>t</u> represents a translational displacement from the origin. If the symmetry operations are restricted to those which preserve bond lengths and bond angles, <u>R</u> is a real orthogonal matrix which can be expressed as:

$$\frac{\mathbf{R}}{\mathbf{R}} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{bmatrix}$$

The notation commonly adopted to express a rotation followed by a translation is :

$\{\underline{\alpha} \mid \underline{t}\}$

 $\underline{\alpha}$ is the operator for proper or improper rotation, i.e. those which involve a pure rotation, and a rotation plus inversion about a centre respectively; <u>t</u> is the vector of translation.

The combinations of the type $\alpha \mid 0$ involve no translational

motion and all symmetry elements pass through a point and form the "point group" of collection of atoms concerned. Combinations involving t are termed "space groups". The vector t is composed of a set of three translations in the x, y and z directions such that:

$$t_n = n_1 t_1 + n_2 t_2 + n_3 t_3$$

 n_1 , n_2 and n_3 are integers, and \underline{t}_1 , \underline{t}_2 and \underline{t}_3 are called the "basic primitive translations". The translations \underline{t}_1 , \underline{t}_2 and \underline{t}_3 may be used to form a lattice in three dimensions.

Before any further consideration of the unit cell, it is desirable to consider what are known as Bravais lattices. Such a lattice is an infinite collection of points which have exactly the same environment in the same orientation. A real crystal cannot have an infinite lattice but as the sizes of the atoms are very small, a crystal comprises an infinite lattice to a good approximation. It has been shown that there are only 14 such Bravais lattices and they are shown in figure 1.4. It is not necessary that the centre of every atom in a real crystal corresponds to a point of a Bravais lattice, nor is it necessary that Bravais lattice points should be occupied at all. Each Bravais lattice may be assigned to a crystal system. The labels P, I, F and C stand for primitive, body centered, fully face centred, and centred respectively, the label R is also primitive (Rhombohedral).

Each point of a Bravais lattice contains all the symmetry operations of the point group of the holosymmetric class of the FIG.1.4



crystal system. Table 1.1 contains the point groups of the crystal systems in column 3; the last point group in each system is the holosymmetrical class. There are only 32 point groups, each is a holosymmetrical point group of the crystal class, or a sub-group of one of these.

If we now return to the unit cell, the parallelipiped may be constructed from the basic primitive translational vectors \underline{t}_1 , \underline{t}_2 and \underline{t}_3 . If these vectors are selected in such a way that the unit cell exhibits the symmetry of one of the Bravais lattices it is possible that the unit cell, if it contains more than one point, may not then be primitive. Where there exists a possibility of a primitive and a non-primitive unit cell a relationship can always be established between the two. Unit cells which have labels C, F and I have 2, 4 and 2 times the volume of the corresponding primitive unit cell respectively.

Symmetry elements of a space group which are not pure translations may involve translation and rotation or translation and reflection. Because of the constraints imposed by the ordering within a crystal, it is necessary to introduce additional symmetry elements to relate identical "sites" in the unit cell or in adjacent unit cells. Such symmetry elements are called screw axes and glide planes. An 'n' fold screw axis consists of a $2\pi/n$ rotation followed by a translation of $\frac{1}{n}$ times the unit cell length in the direction of the axis. A glide plane consists of a reflection in

8.

a plane, followed by a translation of half a unit cell length along the plane. Figure 1.5 illustrates the concept of screw axes and glide planes. In space groups limitations are placed on the values θ can take in the rotational matrix <u>R</u>. The values of θ allowed are $\pi/_2$ and $\pi/_3$. The result is that the number of different space groups is limited to 230. Each space group can have a "factor group" associated with it. This group is the space groups less the translational elements, and is isomorphous with a point group. The factor group of any space group is immediately obtained from the Schonflies symbol of the space group. For example, space group P222 (no 16) \equiv D_2^1 in Schonflies notation, the relevant factor group is D_2 from point group tables.

In addition to the 230 space groups which are concerned with lattices in 3 dimensions, Wood (1964) has shown that there are 80 "diperiodic groups". These groups are each related directly to a space group (as they are a sub-group of a group). The diperiodic groups, unlike the 17 strictly two-dimensional groups given in volume 1 of "International Tables for X-ray Crystallography", are concerned with lattices which are periodic in only two dimensions but admit that symmetry operations are possible in the third dimension. Such groups are very useful in considering sheet structures, where there are two dimensional lattices which have no chemical bonding between layers. The equivalent of the Bravais lattices, the 5 two-dimensional nets, for these groups are shown in figure 1.6. Each of the 80 diperiodic

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+

FIG. 1. 6





groups can be derived directly from the 230 space groups by inspection. Wood has listed the sites allowed for each of these groups and has retained the nomenclature given in I.T.X.R.C. These groups are considered in more detail in the last chapter of this thesis.

Modes of Vibration in Crystals

An isolated non-linear polyatomic molecule has 3n-6 vibrational modes associated with it, where n = the number of atoms. In considering a crystal it would be necessary to take into account N unit cells each containing n atoms; this yields 3nN modes as translations and rotations cannot be ignored in solids. It is immediately obvious that an astronomical number of modes would be predicted. Fortunately, simplifications can be made. The vibrational modes of crystals can be thought of as combinations of identical vibrations in all the unit cells. The quantum of energy which describes unit excitation of one of these standing waves is called the "phonon".

Using the established equation:

$$E = mc^2 = \frac{hc}{\lambda}$$

mc = $\frac{h}{\lambda}$ mc is a momentum term and is described by the vector quantity \vec{P}

 $\vec{P} \alpha \frac{1}{\lambda}$

We can now relate $\stackrel{\frown}{P}$ to a generalised vector (K) and describe K by the equation

$$K = \frac{2\pi}{\lambda}$$
 (1) K is called the wave vector

As the velocity of electromagnetic radiation in a vacuum is a constant (C) and is related to frequency (W) and wavelength (λ) by:

$$C = W\lambda$$

from (1) above Kal therefore the frequency of a phonon can be related to K by:

$$W = 2\pi CK \quad \therefore \quad K \alpha W \qquad (2)$$

If a crude model is adopted, and the example of a very simple vibrating system is taken. A restoring force (F) can be expressed in terms of the displacement x.

 $F = ax + bx^2 + cx^3 + \dots$

If x is sufficiently small the first term predominates and the vibration is simple harmonic. Higher terms are used to describe anharmonicity, a description of which will not be attempted here. In the case of atomic lattices, no one vibration may be isolated from the others. These vibrations can then be described in terms of normal modes, each possessing an angular frequency (W) and wave vector (K). Each mode can therefore be quantised into phonons of energy W and momentum K.

From (1) above λ is the wavelength of the phonon. The relation between frequency and K is called a dispersion relation. Born and Huang (1954) have proved that for unit cells containing more than one atom K has two branches, known as acoustic and optic branches. Figure 1.7 shows such a dispersion relation. The optic branch has three branches, two T.O. (transverse optic), modes, and one L.O. (longitudinal optic) mode. The acoustic branch has two branches, one T.A. (transverse acoustic) mode and one L.A. (longitudinal acoustic) mode. At values of K & O the two T.O. modes are degenerate, this is streated in greater detail in Chapter two; in addition the acoustic branch has effectively zero frequency and corresponds to the bulk translations of the unit cell along the x, y and z directions. At K = 0 the modes predicted to occur are known as the "fundamental modes of vibration" or "factor group fundamentals"; these correspond to all unit cells vibrating in phase. Figure 1.8 shows that for all cells vibrating in phase the wave vector of the phonon is very small and the wavelength is large.

For the purposes of i.r. and Raman experiments the radiation has a frequency of no more than 2×10^4 cm⁻¹, so that the wave vector of the radiation is $< 2 \times 10^5$ cm⁻¹. When a photon and a phonon interact the wave vector must be conserved, so that

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Figure 1.7

 W_L = L.O. frequency W_T = T.O. frequency

L.O. is the longitudinal optic mode.

T.O. is the transverse optic mode.

L.A. is the longitudinal acoustic mode.

T.A. is the transverse acoustic mode.

FIG.1.7

A Dispersion relation



the phonon in i.r. or Raman experiments is also $< 2 \times 10^5$ cm⁻¹. This is much smaller than the largest phonon wave vector possible (π/d) where d is the lattice spacing) which is of the order of 10^8 cm⁻¹. Figure 1.8 shows that at K = 0 the phonon will have infinitive wavelength and all unit cells will be vibrating in phase. Phonons with wave vector $\sim 10^5$ cm⁻¹ have a frequency of the same order as the infinite wavelength phonon. The assumption normally made in i.r. and Raman experimentation is that K = 0. This is the basis of the vibrational analysis used here, where only one unit cell (the primitive unit cell) is considered. The wavelength of the radiation is large in comparison to the size of the unit cell, so this assumption is justified.

In an identical manner to which the unit cell was constructed from three translational vectors \underline{t}_1 , \underline{t}_2 and \underline{t}_3 , it is possible to define a set of reciprocal lattice vectors, g_1 , g_2 and g_3 to construct the first Brillouin zone of the lattice.

$$g_{1} = \frac{2\pi(\underline{t}_{2} \times \underline{t}_{3})}{\underline{t}_{1}(\underline{t}_{2} \times \underline{t}_{3})}$$
$$g_{2} = \frac{2\pi(\underline{t}_{3} \times \underline{t}_{1})}{\underline{t}_{2}(\underline{t}_{3} \times \underline{t}_{1})}$$

$$g_3 = \frac{2\pi(\underline{t}_1 \times \underline{t}_2)}{\underline{t}_3(\underline{t}_1 \times \underline{t}_2)}$$

the position vector g of any point in reciprocal space may be given in terms of

FIG. 1.8 Unit cell vibrations in a crystal





$g_n = n_1g_1 + n_2g_2 + n_3g_3$

where n1, n2 and n3 are integers.

A paralellipiped in reciprocal space may therefore be constructed, the coordinates of any point are given in terms of K_x , K_y and K_z . The so-called zone centre is the point at which K = 0 and is given the special symbol Γ . The first Brillouin zone or simply Brillouin zone contains all the wave vectors K of the unit cell. Much of the nomenclature relevant to Brillouin zones has been established by Koster (1963), and a mathematical treatment of Brillouin zones is given by Bradley and Cracknell (1972). Just as a unit cell has points of special symmetry, the Brillouin zone also has points of high symmetry each of which is given a special symbol. Multi-phonon modes, i.e. those which are not factor group fundamentals can sometimes be related to these special symmetry sites, a treatment of which will not be attempted here.

Calculation of Factor Group Fundamentals

The method of calculation was first described by Bhagavantam and Venkataray**u**d**u** (1939, 1941, and 1969). The procedure is essentially the same as that of point group analysis. The atoms which comprise a unit cell form the "molecule" for analysis. It is essential only to find the number of equivalent positions under each factor group symmetry operation. It is essential
that only the primitive unit cell is used or more than the required number of modes is predicted.

The method is known as factor group analysis or F.G.A.; it is possible using this method to distinguish between internal modes of the lattice, i.e. vibrations and the translations and rotations of any complex ions (the external modes). A fuller account of the method is given in the last chapter where a simplified F.G.A. scheme is given for the 80 diperiodic groups in three dimensions. It is obvious that a large amount of tedious arithmetic is involved. A revised method described by Newton (1970) and published as a set of tables (Adams and Newton 1970) is available for the 230 space groups, whereby the irreducible representations for any lattice may be directly read without calculation. It is essential only to know the Wyckoff notation of the sites occupied by the atoms in the structure, and that the axes chosen are the "standard set" given in "International Tables for X-kay Crystallography". The equivalence between axes is given in the appendices of volume 1 of the I.T.X.R.C. tables.

An alternative approach to the calculation of the factor group fundamentals is to use the correlation method. This method was first described by Halford (1946) and was shown to be equivalent to F.G.A. by Hornig (1948). From the irreducible representation of a complex ion or molecule correlation tables are used

to observe the changes of symmetry species which occur on correlation to the site occupied by the "centre of gravity" of the complex ion. This so-called site field is the symmetry of the field acting on the complex ion by virtue of its environment. Correlation to the factor group symmetry of the lattice then yields the symmetry species for the internal modes. The coupling between complex ions in a unit cell is responsible for this last assignment of symmetry species. In a simple case a bimolecular unit cell will couple to give in phase and out of phase components for the vibrations of the isolated complex ion. Davydov splitting is the term given to the frequency range of the split between modes of identical type in the crystal. The larger the frequency range the greater the interaction between the complex ions. The correlation method is useful in predicting the intensity of modes expected. A mode which is inactive in a complex ion, but which gains activity by virtue of the site field can reasonably be presumed to be weak; a mode which is active in the complex ion can be presumed to be a strongly allowed mode. F.G.A. gives no indication of the origin of the modes predicted and it is useful to use both methods so that absences in spectra may be explained on the basis of the site field. It is possible in certain circumstances to make the assumption that a distinction between internal and external modes is possible. For the case of molecular crystals where there is very little interaction between molecules; the interatomic forces are very much greater than the long-range

forces between molecules, it may be possible to distinguish the internal modes from the external modes which are expected to occur at much lower frequency. The class of structures which may be called complex ions will have much larger interactions between them and the regions of the spectrum where they occur may well overlap considerably. In addition it is possible that the modes may become mixed, where atomic displacements are similar modes of the same symmetry species may interact. In the extreme case of ionic lattices such a distinction is impossible since the bonding between atoms has very little directional character and the long range forces between atoms may be very large indeed. The notation of translatory, rotatory and internal modes may be reserved only for accounting purposes unless isotopic data is available which proves beyond doubt that a particular mode can be assigned.

The Indicatrix

Light has a sinusoidal wave motion transverse to its propagation direction in two mutually perpendicular planes. One of these sinusoidal motions is the magnetic vector and will be disregarded for the purposes of this thesis since the effects produced by it are not significant in the work reported here. The other wave motion is the electric vector, the direction of which is hereafter called the polarization direction. The

term light is taken to refer to all parts of the electromagnetic spectrum, not only the visible region.

The optical properties of all crystal systems, excluding in most cases cubic crystals, are anisotropic, i.e. vary with orientation. One property which is particularly dependent upon the symmetry of the lattice is the refractive index (n). When light is incident upon the boundary between two layers of differing refractive indices, refraction occurs, unless incidence is normal to the boundary. Crystals have differing refractive indices associated with the crystallographic axial directions, except cubic crystals. However, even in the case of normal incidence for crystals the light is split into two rays. This phenonmenon is known as "double refraction". The refractive indices of crystals show dispersion, i.e. vary with wavelength, however this effect is sufficiently small to be ignored for the purposes of vibrational spectroscopy.

Double refraction may occur in one of two forms for all crystal systems except the cubic system, which is isotropic and does not exhibit double refraction. The two cases are uniaxial and biaxial crystals. For uniaxial crystals the two rays produced are known as the ordinary and extraordinary rays. The ordinary ray is undeviated from its path, the extraordinary ray is deviated from the plane of incidence. Both rays travel through the crystal with electric vectors polarized in mutually perpendicular

directions, and with differing phase velocities. For biaxial crystals both rays are extraordinary. Both rays are polarized in mutually perpendicular directions and have differing phase velocities. Figure 1.9(a) demonstrates the concept of double refraction in uniaxial and biaxial crystals. The two rays may interact to produce interference, this is used as an analytical method by geologists and is known as birefringence; an account is given by Cox, Price and Harte (1967).

The Indicatrix is the term given to the three dimensional representation of the refractive properties of crystals. Walhstrom (1960) has shown that this takes the form of an ellipsoid of revolution. For light incident from any direction the refractive indices and polarization of the two rays produced are given by the magnitudes and directions of the semiaxes of that section of the ellipsoid normal to the direction of incidence.

It is useful at this stage to introduce a term known as the "optic axis". Uniaxial crystals have one optic axis, biaxial crystals have two optic axes. Optic axes are the directions normal to which the sections of the indicatrix ellipsoid are circular. Light incident along these directions is isotropic and is not doubly refracted. The ellipsoid of revolution for uniaxial crystals has one axis of revolution, which corresponds to the optic axis. The ellipsoid of revolution of biaxial crystals is a triaxial ellipsoid. Figure 1.9(b) shows the three

FIG. 1.9 (a)



principal sections of the ellipsoid for biaxial crystals. The three axes of revolution may be related to two-fold axes of symmetry in some crystals classes, this is discussed in greater detail later; the optic axes are not fixed by any symmetry and their position is not usually of concern for single crystal spectroscopy.

The optic axes for uniaxial crystals corresponds to the three, four or six-fold axis of symmetry of trigonal, tetragonal and hexagonal crystal systems respectively. The three two-fold axes of symmetry of the biaxial ellipsoid may be related to twofold axes of symmetry of orthorhombic and monoclinic crystals; triclinic crystals are also biaxial, but the two-fold axes are not related to any symmetry elements as triclinic crystals may have only a centre of inversion as a symmetry element. For orthorhombic crystals the three axes of the ellipsoid are the three two-fold axes of symmetry of the system. For monoclinic crystals one axis of the ellipsoid is the unique axis of the system, the other two axes need not correspond to other two fold axes although they are required to be coplanar with them.

The three two fold axes of the biaxial ellipsoid are directions along which no double refraction occurs, as these correspond to the vibration directions of the extraordinary rays produced by double refraction. Radiation polarised parallel to one of these directions will therefore not be doubly refracted as no component of the radiation exists which can produce another ray.

In conclusion, the optical properties of crystals may be of use to determine the axes of the crystal. A polarising microscope is used to determine the position of axes within a crystal; this is essentially the same as an ordinary microscope but it has two polarisers set at 90° to each other. One polariser is mounted in the collimator of the light beam which passes through the optics, the other polariser is mounted in the eye-piece. If a crystal is rotated on the microscope stage with both polarisers in place it will be seen that in certain orientations there is total extinction of light passing through the crystal. Along these directions the light is not doubly refracted, therefore the initial polarisation of the light is maintained. This light cannot be observed with the second polariser in place as the polarisation directions are mutually perpendicular. It is clear therefore that these orientations locate the optic axis of uniaxial crystals, and therefore the 3, 4 or 6 fold axis of symmetry, and the two fold axes of symmetry of orthorhombic and monoclinic crystals. Thus it is possible to locate the axes of crystals by a simple experiment; this enables the axes to be related to the external morphology which is essential for oriented studies in polarised light.

For uniaxial crystals: trigonal, tetragonal and hexagonal systems, the axis of symmetry is easily located and other axes are perpendicular to this axis, further confirmation is seldom required. For biaxial crystals: orthorhombic, monoclinic and

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triclinic; the indicatrix axes are of use to locate crystallographic axes but they give no indication of which axis is which. A determination in these circumstances must be done by X-ray methods.

An account of X-ray methods of location of axes will not be given here but has been reviewed by Henry, Lipson and Wooster (1954), and Stout and Jensen (1968).

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Chapter Two

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The Practical Investigation of Crystals

Section A

A Review of I.r. Reflectance Spectroscopy

and Techniques

I.r. Spectroscopy

A great deal of the i.r. information collected for this thesis was obtained using the method of reflectance spectroscopy.

The following is an account of the reasons for choosing reflectance methods, the experimental advantages of using the technique and the disadvantages inherent in the method. A review of reflectance methods is given, which includes the theory essential to an understanding of the method. Where possible derivations of formulae are given, in the case of exhaustive mathematical treatments to obtain formulae no derivations are given but references are quoted for further reading. Some account of the history of the development of the technique is also given. The final section deals with the problems encountered with reflectance spectra and the subtle adjustments to data which are sometimes necessary to achieve meaningful analyses.

Reflectance and Transmission Methods

All people who have attempted single-crystal transmission experiments will appreciate the extreme difficulty encountered in preparing the sufficiently thin slices of crystal required. If the crystal absorbs radiation very strongly thicknesses of the order of 1-2 μ m may be necessary, thicknesses of 10-20 μ m are common. If the crystal is air stable, non-hygroscopic and only sparingly solu ble in a non-toxic, non-volatile solvent (e.g. water) thinning the crystal to the final stages of preparation is not difficult, if perhaps extremely tedious. The last stages of preparation are often achieved by polishing on a soft surface to avoid cracking the very thin sample.

Transmission experiments sometimes fail due to some adhesive between the crystal and the transparent medium onto which it is mounted. This may have the effect of increasing sample thickness beyond a critical value, or it may act as a cut-off filter for the transmitted radiation.

Low temperature work can be a lengthy procedure, nearly all infra-red transmitting materials are poor conductors of heat; thus long cooling periods may be necessary to achieve very low temperatures at the sample.

For reflectance measurements, the crystal is mounted directly onto a medium of high thermal conductivity (normally copper) using a quick setting epoxy resin, into which fine aluminium powder has been incorporated in order to increase thermal contact. A crystal once mounted in such a manner is immediately ready for experimental work, unless a small amount of polishing is required first.

If i.r. data are required throughout the entire frequency range (10-4000 cm^{-1}) transmission measurements would be required

with different transparent media. It would be necessary to remove the crystal from one mount for the high frequency range (KBr) and mount again onto the medium for low frequency work (polythene). This can be an extremely perilous operation, the alternative is to mount and thin another crystal. Reflectance does not rely on any transparent media and the same sample may be used for all frequency ranges. Figure 2.1 shows the apparatus used to obtain reflectance data up to 1000 cm⁻¹, using the Beckmann RIIC FS720 interferrometer; other reflectance units are of similar design. The Polyethylene window is removed for ranges above 400 cm⁻¹, when in place, it allows the sample compartment to be evacuated independently of the rest of the machine. This enables beam splitters to be changed during low temperature work.

If hygroscopic or air-sensitive crystals are studied a method is given in this thesis of using reflectance techniques. Hygroscopic samples in extremely thin sections may easily dissolve in the small amount of water produced by evacuating an instrument, by the de-gassing which is encountered. Reflectance spectroscopy has one serious drawback, that is that adsorption frequencies cannot be estimated visually without considerable experience in the technique. However data may be analysed using one of the methods described herein in order to obtain accurate parameters.

FIG. 2.1



I.r. Activity

Mitra and Gielisse (1964) have extensively reviewed this subject and only an account relevant to this thesis is given here.

I.r. activity is associated with the interaction of the oscillating electric vector of the radiation and the oscillating electric dipole present in a molecule or primitive unit cell. If there is a change in dipole moment, i.r. activity will occur, hence homonuclear diatomics which have no dipole moment are not i.r. active. The irreducible representation of a molecule or primitive unit cell is given in terms of symmetry species. If one or more of these species are associated with the translational vectors x, y and z, ir. activity will occur.

If polarised radiation is used, such that the plane of the electric vector of the radiation is incident on a specific orientation of the primitive unit cell; only the component of the dipole which is coplanar interacts strongly. The component of the dipole which is perpendicular to the plane of the radiation has effective_y zero interaction. Thus symmetry species associated with the respective x, y and z vectors of the unit cell can be excited uniquely. This enables the spectrum of a unit cell to be decomposed into bands associated with a symmetry species and a complete assignment is possible.

I.r. activity in crystalline solids is associated with three types of phonons. These are known as Transverse Optic phonons (T.O.) and Longitudinal Optic phonons (L.O.). At the centre of the Brillouin zone where K = 0 the two T.O. modes are degenerate (See figure 2.3(b)). The two T.O. modes correspond to the vibrations of the primitive unit cell when the plane containing the electric vector of the radiation and the dipole moment is perpendicular to the direction of the propagation of the radiation. (See figure 2.2(a)). The Longitudinal optic phonon can be described as the interaction with the radiation of the charge variation on the surface of the unit cell; this oscillates about a position with its own frequency. L.O. modes can be uniquely observed by the technique devised by Berreman (1963), which has also been used by Hargreave (1971). The method entails using oblique angles of incidence on thin films of substrates, usually in contact with highly polished surfaces. If the angle of incidence is sufficiently oblique the electric vector of the radiation is approximately parallel to the surface of the crystal; and is therefore aligned favourably for strong interaction with the surface charge variation (see figure 2.2(b)). L.O. modes can also gain activity in the Raman process where the factor group is non-centrosymmetric (see Chapter 2, section B).

If we confine our attention to angles of near normal incidence, we might reasonably expect that only T.O. modes will be active in the general case. In transmission measurements which use normal incidence, only T.O. modes will be active.





FIG.2.2(b)



(oblique incidence)

FIG. 2.3(a)



FIG. 2.3 (b)



Reflectance Spectroscopy

In order to explain the phenomenon of the interaction of radiation at a plane surface, it is necessary to introduce symbols which represent the microscopic physical effects which occur.

The following are given without derivation:

- P represents the electric polarisation, defined as the dipole moment per unit volume in the medium.
- E is the average electric field within the medium.
- D is the electric displacement caused by the electromagnetic field in the medium.
- D, E and P are related by the following equation

 $D = E + 4\pi P \quad (1)$

We now consider the effect of a monochromatic plane wave of angular frequency w and wave vector K travelling through a crystalline medium. The electric field E of the wave will cause forced oscillations of the atomic particules, a linear relationship between D and E will then exist.

$$\underline{D} = \underline{\varepsilon} \underline{E}$$

Because both <u>D</u> and <u>E</u> are vector quantities $\underline{\varepsilon}$ is a 2nd rank tensor. $\underline{\varepsilon}$ is called the dielectric tensor and has six components represented by (taking x, y and z orthogonal components, which correspond to the crystallographic axes in orthorhombic and higher symmetry systems).

$$D_{x} = \varepsilon_{xx}E_{x} + \varepsilon_{xy}E_{y} + \varepsilon_{xz}E_{z}$$

$$D_{y} = \varepsilon_{yx}E_{x} + \varepsilon_{yy}E_{y} + \varepsilon_{yz}E_{z}$$

$$D_{z} = \varepsilon_{zx}E_{x} + \varepsilon_{zy}E_{y} + \varepsilon_{zz}E_{z}$$

$$(\varepsilon_{xy} \equiv \varepsilon_{yx})$$

Using polarised radiation oriented along the principal axes, non-diagonal terms are zero.

Thus the relations reduce to:

 $D_{x} = \varepsilon_{xx}E_{x}$ $D_{y} = \varepsilon_{yy}E_{y}$ $D_{z} = \varepsilon_{zz}E_{z}$

For tetragonal, hexagonal and orthorhombic systems E must be either parallel or perpendicular to the crystallographic z direction, if non-diagonal terms are to be excluded. For cubic systems (isotropic) $\underline{\epsilon}$ does not vary with orientation. Mostellar and Wooton (1968) have examined the validity of the above relations and reviewed the dielectric theory involved. ϵ can be thought of as the response of the crystal to a perturbing field of frequency w and is therefore itself a function of frequency (see figure 2.3(a)).

If the radiation is absorbed by the medium, there will be a phase difference between D and E by virtue of the finite relaxation time of a vibrational mode. This can be included in the theory by allowing ε to have complex values. Born and Huang (1954) have produced a mathematical treatment of lattice vibrations in which the proof can be found.

Thus ε can be expressed as:

 $\varepsilon = \varepsilon_1 + i\varepsilon_2$ (2)

where ε_1 and ε_2 are the real and imaginary parts respectively of the dielectric tensor.

The refractive index (n*) of a material may be defined as the ratio of the velocity in a vacuum (c) to a phase velocity (V*) in the medium, i.e.

 $n^* = \frac{c}{V^*}$ (3) i.e. $V^* = \frac{c}{n^*}$

Hodgson (1970) has derived from Maxwell's relations a relationship between wave-vector K, dielectric tensor ε and the velocity of electromagnetic radiation in a vacuum (c), with respect to frequency of the radiation (w).

$$c^{2}(K.K) = w^{2}\varepsilon \qquad (4)$$

This is easily rearranged to give

$$\frac{W}{K} = \frac{c_1}{\epsilon^2}$$
 (5)

as $K = \frac{2\pi}{\lambda}$ and $c = w\lambda$, $\frac{w\lambda}{2\pi} = \frac{c}{\epsilon^{1}}$

 $\varepsilon^{\frac{1}{2}}$ is dimensionless. $c/\varepsilon^{\frac{1}{2}}$ is therefore a phase velocity. The similarity with equation (3) may be used to define n* in terms of ε , i.e. n* = $\varepsilon^{\frac{1}{2}}$ or n*² = ε . (6) from n* = c/c.

We have therefore established a link between microscopic quantities (D, E and P) and macroscopic quantities (n) via this relation.

However, it follows that if ε is complex n may also have complex values, i.e.

 $n^* = (n_1 + in_2)$

which is usually expressed in the form

 $n^* = (n_1 + ik)$ (7)

 n_1 is called the refractive index and k the extinction coefficient. (Hereafter for simplicity the nomenclature $n \equiv n_1$ is established) from the form of equations (6) and (7).

$$\varepsilon \equiv (\varepsilon_1 + i\varepsilon_2) \equiv n^{*2} \equiv (n + ik)^2$$

... $(\varepsilon_1 + i\varepsilon_2) = (n^2 - k^2 + 2ink)$

equating real and imaginary parts.

$$\varepsilon_1 = n^2 - k^2 \tag{11}$$

$$\varepsilon_2 = 2nk$$
 (12)

It is therefore clear, that a route has been established to enable the dielectric tensor to be calculated from other parameters. If n and k are known for any frequency (w), the real and imaginary parts of ε may be uniquely established.

Reflectance spectra often include very broad bands, unlike those obtained in transmission measurements. The area of large variation of reflectance with frequency is known as the Reststrahlen region.

During absorption of radiation, the dielectric tensor shows large variations with frequency. Figure 2.3(a) shows that at zero frequency ε has a value denoted by ε_0 . In the region of absorption (bounded by w_T and w_L) ε undergoes a catastrophe for the ideal case (a 100% ionic diatomic lattice). This is explained in classical terms by the introduction of complex values of ε . When the region of absorption has been passed ε returns to a slowly varying function with respect to frequency, and will assume a constant value at infinite wavelength denoted by ε_{∞} . At this limit, it is assumed that ε has real values only and hence from equation (6)

$$\varepsilon_{\infty} = n^2$$
 (k \approx o)

where n = visible light refractive index.

Mitra and Nudelman (1969) have reviewed the link between the quantities ε_0 , ε_{∞} and ε as a function of frequency. They state (for a one oscillator model):

$$\varepsilon = \varepsilon_{\infty} + \frac{(\varepsilon_{0} - \varepsilon_{\infty}) w_{0}^{2}}{w_{0}^{2} - w^{2}}$$
(13)

 w_{o} and w are frequency terms.

Equation (13) is known as the dispersion formula.

From the Fresnel formula:

$$R = \left\{ \frac{(n^* - 1)}{(n^* + 1)} \right\}^2$$
 (14)

where R is the observed reflectance at any wavelength (w), and n is the refractive index at that wavelength.

Using

$$n^* = \varepsilon^{\frac{1}{2}}$$

$$R = \left\{ \frac{(\varepsilon^{\frac{1}{2}} - 1)}{(\varepsilon^{\frac{1}{2}} + 1)} \right\}^2$$
(15)

we have a direct link between ε and the observed reflectance.

From equation (13) when $w = w_0 \varepsilon$ will tend to ∞ . R from equation (15) will tend to 1.

When w is infinitesimally greater than $w_0 \epsilon \rightarrow -\infty$ (R = 1) and will remain negative until a frequency satisfies

$$o = \varepsilon_{\infty} + \frac{(\varepsilon_{0} - \varepsilon_{\infty}) w_{0}^{2}}{w_{0}^{2} - w^{2}}$$

which is w = $(\epsilon_0/\epsilon_{\infty})^{\frac{1}{2}}W_0$

In this case $\varepsilon = o$ therefore $R \rightarrow o$.

Figure 2.4(a) illustrates this theoretical phenomenon $(\gamma/w_0 = 0.00)$. The values of w for w_0 and $(\varepsilon_0/\varepsilon_{\infty})^{\frac{1}{2}}w_0$ correspond to w_T and w_L of figure 2.3(a) and are the T.O. and L.O. frequencies respectively.

In practice this effect is never seen because of a parameter known as damping. In the absence of anharmonicity, i.e. a system which conforms to classical simple harmonic motion, damping introduces a mechanism whereby energy can leak out of the vibrational modes into other modes, and as such is a function of the lifetime of both T.O. and L.O. modes. Thus it may be reasonably expected that the lifetimes of these modes will influence the shapes of the reflectance curves obtained.

Cochran (1973) has given a brief account of the concept of damping. Damping can be conceived as a frequency dependent

FIG. 2.4 (a)



FIG. 2.4(b)



variable; in the classical sense, it is described however as a single constant value γ , which is often scaled γ/w_0 for convenience (Mitra 1963).

Figure 2.4(a) shows the effect of changing the value of the constant γ/w_0 in a synthetically generated spectrum, and illustrates the unreliability of visually estimating the T.O. frequency (which remains constant throughout).

The frequency dependence of γ has been examined by Gervais and Piriou (1974). Using a semi-quantum model they have deduced the dependence of damping, as a function over all frequencies and temperatures, in this case damping is given by symbol Γ to distinguish it from the classical constant value.

Denham and Field <u>et al</u> (1969) have used a frequency dependent damping function, based on quantum mechanical arguments by Cowley (1963). Using the real and imaginary parts of the dielectric tensor, along with the constants ε_0 and ε_{∞} the damping function can be expressed as

$$\Gamma_{(w)} = \frac{(\varepsilon_0 - \varepsilon_{\infty})w_0}{2} \frac{\varepsilon_2(w)}{(\varepsilon_1(w) - \varepsilon_{\infty})^2 + \varepsilon_2^2(w)}$$

Mitra (1963) has shown that for a classical damping (γ) the values of γ/w_0 are linear to a very good approximation with respect to the maximum value of the reflectance function.

Figure 2.4(b) shows the variation of γ/w_0 with respect to $1/R_{max}$ calculated from figure 2.4(a). The concept of a single value for γ is the one adopted here for reflectance analysis.

It remains to be established how the exact value of the T.O. frequency can be obtained. The L.O. frequency in the case of centrosymmetric solids does not assume such importance, as these are inactive in i.r. transmission and are therefore not observed.

Two such methods exist for <u>routine</u> analysis of samples. a) what has become known as Kramers-Kronig analysis (k-k), b) classical dispersion analysis (C.D.).

Kramers-Kronig Analysis

The phenomena of absorption and the phase shift of waves has been known for some time. Kramers and Kronig independently discussed the application of some of the known relations to optical absorption.

The significance of the real and imaginary parts of the dielectric tensor become apparent when the variation of these with frequency is established. Simon (1951) demonstrated a proof that the maximum of the imaginary part of the dielectric tensor (2nk) corresponds to the T.O. frequency. Similarly the node (=0) of the real part of the tensor corresponds to the L.O. frequency. Therefore what is required is to establish the variation of n and k with frequency. The functions ε_1 and ε_2 can then be calculated for any frequency and the T.O. and L.O. established.

Simon (1951) gives one of the first accounts in the literature of the study of materials by reflectance. In the absence of more sophisticated methods, it was necessary to collect data at two angles of incidence. Simultaneous equations were then used to solve unique values for n and k at any particular wavelength. In order to by-pass the tedium of a great deal of routine calculation, Simon used a graphical method of analysis. It is interesting to note that Simon observed distortions of the observed reflectivity at large angles of incidence i.e. $\chi70^{\circ}$, remembering the Berreman method of establishing L.O. modes at oblique incidence. Simon reported the difficulty of obtaining reflectance measurements at oblique incidence, but concluded that the technique showed promising results.

The determination of the optical constants n and k from one set of data collected at near normal incidence was first discussed in detail by Robinson (1952). The method used to obtain the i.r. spectrum of P.T.F.E. by Robinson and Price (1953); however, graphical solutions were still necessary. The conclusion to the paper indicated that some form of computation was necessary to make the method easier to use in a routine manner.

The one angle of incidence technique is made practical by studying the phase change on reflection of the reflected wave. Bowlden and Wilmshurst (1963) have extensively reviewed the technique and tested the results obtained for errors in the input data. They concluded that the results were of the same order of accuracy as low resolution absorption experiments.

The phase change on reflection (θ) is related to the observed reflectance (R) and the amplitude coefficient (r) by:

$$(R)^{\frac{1}{2}} = re^{i\theta} \qquad (16)$$

Bowlden and Wilmshurst have shown by the application of the Cauchy theorem, that θ can be related **d** rectly to $(R)^{\frac{1}{2}}$ by

$$\theta(w^{-}) = \frac{2w^{-\theta}}{\pi} \int_{0}^{\infty} \frac{\ln(R)^{\frac{1}{2}}(w) - \ln(R)^{\frac{1}{2}}(w^{-})}{(w^{2} - w^{-2})}$$
(17)

using the Kramers-Kronig dispersion relations (Kronig (1926) and (1929)), and that the optical constants n and k can be derived from Θ by the following relations:

$$n = \frac{1-R}{1+R-2(R)^{\frac{1}{2}}Cos\theta}$$
(18)

$$k = \frac{-2(R)^{\frac{1}{2}} \sin \theta}{1 + R - 2(R)^{\frac{1}{2}} \cos \theta}$$
(19)

The phase angle θ may show minor discrepancies due to the

magnitude of $(R)^{\frac{1}{2}}$ at all other frequencies. It is here that the small errors in θ have to be catered for in adjustments to the reflectance spectrum in analysis.

Figure 2.5 shows the parameters obtained from a K-K analysis. The L.O. mode frequencies are established from the real part of the dielectric function (labelled ε ' by convention) and the T.O.s from the maximum of the imaginary part function (ε " by convention).

The variation of n and k will be discussed later.

Classical Dispersion Theory

The dispersion formula (equation 13) may be re-written to include a damping term (Nudelman and Mitra 1969).

For a simple harmonic oscillator:

$$\varepsilon(w) = \varepsilon_{\omega} + \frac{(\varepsilon_{o} - \varepsilon_{\omega})}{1 - (W/W_{o})^{2} - i(\gamma/W_{o})(W/W_{o})}$$
(20)

This equation is now complex, but will generate realistic reflectance spectra for suitable values of $\varepsilon_{0}^{}$, $\varepsilon_{\infty}^{}$, $w_{0}^{}$ and γ .

Damping must be included or the reststrahlen region would resemble figure 2.4(a) (γ/w_{0} = 0.00).

Equation (20) can be expanded in terms of real and imaginary parts to obtain ϵ ' (real function) and ϵ " (imaginary function) to give


$$\varepsilon' = n^{2} - k^{2} = \varepsilon_{\infty} + \frac{(\varepsilon_{o} - \varepsilon_{\infty})(1 - (W/W_{o})^{2})}{(1 - (W/W_{o})^{2})^{2} + (\gamma/W_{o})^{2}(W/W_{o})^{2}}$$
(21)

$$\varepsilon'' = 2nk = \frac{(\varepsilon_{O} - \varepsilon_{\omega})(\gamma/W_{O})(W/W_{O})}{(1 - (W/W_{O})^{2})^{2} + (\gamma/W_{O})^{2}(W/W_{O})^{2}}$$
(22)

Seitz (1940) gives an alternative form by introducing a parameter known as oscillator strength. This is effectively a measure of the width of a band between T.O. and L.O. frequencies.

$$\varepsilon' = \varepsilon_{\infty} + \left(\frac{B_{j}(w_{0}^{2} - w^{2})}{(w_{0}^{2} - w^{2})^{2} + \gamma^{2}w^{2}} \right)$$
(23)

$$\varepsilon'' = \left(\frac{B_{j} \gamma W}{(W_{0}^{2} - W^{2})^{2} + \gamma^{2} W^{2}}\right)$$
(24)

 B_{j} is the oscillator strength of an oscillator j at T.O. = w_{0} and damping = $\gamma.$

For multi-oscillator problems this is the more convenient form to use and the bracketed expressions must be summed over all oscillators.

Classical dispersion analysis involves the generation of a spectrum using equations 21-24, and the subsequent variation of parameters to obtain a good fit with observed data. Final values then correspond to the parameters of the observed oscillator.

It is immediately obvious that this task is almost impossible without the aid of an iterative routine which adjusts parameters automatically in the computer program used. The monitoring of the progress is done by calculating functions ε ' and ε " and solving for n and k (a trivial task) and then the reflectivity at any wavelength is calculated via a revised Fresnel formula.

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$
(14b)

 n^* in the original formula (14) is replaced by (n + ik). In regions of transparency k & 0 and the equations are identical.

Spitzer and Kleinman (1963) used the damped simple harmonic oscillator model to reproduce the reflectance spectrum of \propto quartz. Barker and Hopfield (1964) reported however, that the model failed to predict the dielectric behaviour of some Perovskite structure oxides, and determined the reason for failure as the non-dependence of the damping function with frequency.

Andermann, Caron and Dows(1965) suggested a frequency dependent correction term to θ . The basic assumption was that the phase angle θ can be split into components.

$$\theta = \Delta \theta_{\rm L} + \theta_{\rm (W_{o})} + \Delta \theta_{\rm u}$$

 $\theta_{(w_0)}$ represents the contribution to θ at any frequency, from the reflectivity over the entire range of absorption of radiation and as such is equivalent to equation (17).

 $\Delta \theta_{\rm L}$ and $\Delta \theta_{\rm u}$ represent respectively the contribution to θ from the regions below the lowest oscillator and above the highest oscillator, regions of transparency.

 $\Delta \boldsymbol{\theta}_{L}$ and $\Delta \boldsymbol{\theta}_{u}$ were evaluated as:

$$\Delta \theta_{\rm L} = \frac{1}{2\pi} \int_{0}^{W_{\rm O}} \int (\ln r_1 - \ln r_2) \{ \frac{\ln(w_1 - w_2)}{(w_1 + w_2)} \}$$
(25)

Subscript 1 represents the first data point. Subscript 2 represents all other data points up to w_0 .

$$\Delta \theta_{\rm u} = -\frac{1}{2\pi} \int_{W_{\rm o}}^{\infty} \int (\ln r_3 - \ln r_4) \{ \frac{\ln(w_3 - w_4)}{(w_3 + w_4)} \}$$
(26)

Subscript 3 represents the highest data point taken. Subscript 4 represents all other data points from w_0 to the last point.

Use of equations (25) and (26) partially overcomes the difficulties associated with a non-variable damping function, and the imperfections introduced by it.

Verleur in a review (1968) showed how effective the simple harmonic oscillator model can be at determining optical constants over a very limited range. This was effected by assigning additional oscillators (which need not correspond to real oscillators) outside the range studied, in order to fit the observed reflectivity spectrum and thus obtain the parameters required.

Gervais and Piriou (1974) have extended the simple harmonic oscillator model, using a semi-quantum model. In this system L.O. modes are taken into account along with T.O. modes, thus an estimate of oscillator strength is no longer needed.

$$\varepsilon = \varepsilon_{\infty} \prod_{j} \frac{w_{j(L.0.)}^{2} - w^{2} - i\gamma_{j(L.0.)}^{W}}{w_{j(T.0.)}^{2} - w^{2} - i\gamma_{j(T.0.)}^{W}}$$
(27)

is the form used.

 $w_{j(L.0.)}$ and $\gamma_{j(L.0.)}$ are the L.O. frequency and damping term respectively.

 $w_{j(T.0.)}$ and $\gamma_{j(T.0.)}$ are the T.O. frequency and damping term.

A program has been devised in this laboratory to utilise the method of equation (27) and produced a high consistency with observed data.

An essential pre-requisite of classical dispersion analysis is to do a Kramers-Kronig analysis initially, to establish T.O. frequencies and the damping function. Although $\gamma/w_0 \propto \frac{1}{R_{max}}$ (Mitra 1963), the band width at $\frac{1}{2}$ peak height of the ε " maxima = 2Γ and thus the damping term may be calculated accurately. Calculated values can then be compared with those obtained from K-K analysis for accuracy.

Information obtained from Reflectance Analysis

The programs written as an integral part of this thesis all output the following parameters as a function of frequency.

a) observed reflectance

b) refractive index (n)

c) extinction coefficient (k)

d) real part of the dielectric tensor (ϵ ')

e) absorption coefficient (α)

f) conductivity (σ)

g) imaginary part of the dielectric tensor (ε ")

Of these, two have not yet been described.

i) Absorption coefficient (**\alpha**): This is calculated from the extinction coefficient (k) by the following equation.

 $\alpha = 4\pi k/\lambda$

where λ = wavelength of the radiation in a vacuum and is approximately equal to c/w, where w is the frequency of the radiation. α may be used in the familiar Lambert's law:

 $I_x = I_o exp(-\alpha x)$

where I_{o} is the intensity of the incident ratiation. I_{x} is the intensity of the radiation after traversing x cms, the depth of penetration can be found if I_{o} and I_{x} are calculated.

ii) Conductivity (σ) : This is calculated from the refractive index and extinction coefficient by the relation:

 $\sigma = nkw = \varepsilon''w/2$

The conductivity can be used to calculate T.O. frequencies. However, it has a far more significant use. It has been shown (Hodgson 1970) that σ is a complex quantity, the real part of which can be used to calculate power absorbed. Peaks in the conductivity spectrum at greater than the L.O. frequencies, correspond to two phonon processes.

A useful check on the calculated frequencies of the T.O. and L.O. modes can be performed by overlaying the spectra of n and k (n and k must have the same ordinate expansion factor).

The number of cross-over points locate alternatively the T.O. and L.O. modes (as shown in figure 2.5). This has become known as Drude's rule (Renneke and Lynch 1965). This rule is often abused, as when oscillators of widely varying intersites are present, n and k frequently do not show sufficient points at which they have the same value. Chang and Mitra (1968) have reviewed this method and concluded that it is only suitably applied when a few oscillators of approximately equal strength are present.

If all the T.O. and L.O. frequencies are established using

the methods of ε " maxima, ε ' nodes and n, k cross-over points, none remaining unfound, the radio frequency dielectric constant may be calculated (ε_0).

The extended Lyddane-Sachs-Teller relationship (Lyddane, Sachs and Teller 1941) (Casselman, Mitra and Spector 1965) relates $\varepsilon_{o}, \varepsilon_{\infty}$ to the T.O. and L.O. frequencies as follows.

$$\left| \right|_{i} \frac{T.0.i}{L.0.i} = \left(\frac{\varepsilon_{0}}{\varepsilon_{\infty}} \right)^{\frac{1}{2}}$$

This is the only reliable method of calculating ε_0 , as the reflectance at low frequencies is seldom known accurately, therefore equation (15) cannot be strictly applied.

The damping factor γ as already stated is found from the width at half-peak height of ε ". γ is inversely proportional to the lifetime of the T.O. mode :

 $\gamma \propto \frac{1}{T}$ where T = lifetime of the mode

Thus ratios of lifetimes may be calculated, which may provide useful data for theoretical studies of the compound.

Reflectance spectroscopy can therefore provide information which would be difficult to obtain by other means, and is useful not only for determining oscillator frequencies, but for collecting data for theoretical studies on the compound under examination.

Modification of Data

In order to do either a K-K or C.D. analysis the observed reflectance must be measured as a function of frequency. This is an extremely tedious procedure, and can be made more efficient by the use of a transparent sheet calibrated vertically with lines at 2 cm⁻¹ intervals, and horizontally with lines at 1% reflectance intervals. The value of the reflectance at any frequency can then be read-off directly to a reasonable degree of accuracy. There are certain areas of the reflectance spectrum where either; the reflectance changes greatly over a very short frequency range, or, the reflectance changes only marginally over a wide frequency range. In these areas it may be necessary to introduce an additional scale for greater accuracy.

Figure 2.6(a) shows the "critical" areas of the reflectance spectrum, i.e. areas as mentioned above where a high degree of accuracy in measuring reflectance is required. It will be found on analysis that neglect of accuracy in these areas will have the inevitable result of impossible values for the ouput parameters. The best guide to the accuracy of the results of analysis is the value of k. In the regions of transparency, k will assume values very close to zero. In the area of intense reflectance, k will assume fairly large positive values (these rarely exceed 10.0). Under no circumstances will k ever be negative in correct analyses. Negative values of k will generate negative values of ε ", this will induce distortions to the frequency variation, with the result that the T.O. frequency will appear to shift from its true position, thus making the entire analysis void.

It is sometimes found, however, that even on taking the most extreme care in measuring the variation of reflectance (values of R as low as 0.01% are possible on the high frequency side of the L.O.), that negative values of k are still generated.

The fault lies within the original data, and subtle corrections are needed in order to generate positive values of k.

Two general situations frequently generate negative values of k :

a) spectra where very low absorptions occur, i.e.<90 cm⁻¹

b) spectra where there are two or more oscillators in very close proximity to one another, of differing intensity.

Other situations arise from time to time. However, the modifications to these two types of spectra can be extended to other examples.

a) The case where low frequency absorptions occur:

The errors arising from these spectra are frequently due to restricted information concerning the value of the reflectance at low wavelengths. The value of R at zero frequency may not be

known to any degree of accuracy due to the lack of energy available. Two principles must be observed.

- i) the % R spectrum must be parallel to the abscissa in the limit where $w \rightarrow o$.
- ii) the % R spectrum must be a smoothly varying function with frequency, sudden increases in R will generate negative values of k.

Smoothing of the reflectance shape, and adjustment of the value of R at w = o can then take place. It must be stressed that the exact amount of smoothing is determined largely by experience. However, the area of intense reflectance must not be altered in position, nor must the area where the gradient rises steeply be tampered with. A cure is most often provided by smoothing at the point of largest curvature (see figure 2.6(b)).

The correct value for R at w = o is found from the value of ε " at $w \simeq o$. If the value for R is too high ε " will have values of the order 0.5-1.0. If the value for R at w = o is too low, ε " is slightly negative and changes slowly to positive values as the region of the T.O. is approached. If the value for R is correct, ε " will have values of the order 0.01.

b) The case where two or more oscillators are close together:

This situation is by far the most difficult to correct as no hard and fast rules apply. However, certain guide lines have

FIG. 2.6a



FIG. 2.6b



been established. In the case of a one oscillator analysis, the % R curve is seen to become parallel to the abscissa as the L.O. is passed (see figure 2.5). When two oscillators are widely spaced there is also a region where the % R curve may not be parallel to the abscissa, but increases very gently with increasing frequency until the next oscillator is approached (see figure 2.7(a)).

It can be imagined that as the two oscillators approach each other this region undergoes a steady compression until the L.O. of the first mode tails over and the reflectance begins to rise steeply for the next oscillator (see figure 2.7(b)). A "critical area" is then established, the section of this area which often requires attention, is the part where the gradient begins to rise gently. Some correction may be possible by introducing a small plateau where the reflectance briefly levels out before beginning to rise steeply - as shown. The amount of smoothing here has been exaggerated to show the concept of smoothing in this area. The exact amount of smoothing can only be determined by trial and error, but only the most subtle amounts will not affect the input data. Large distortions of observed data will invariably introduce errors in θ and hence errors will arise in the computed values of n and k.

In the situation of oscillators in close proximity to each other of widely different intensity (see figure 2.8) another guide line has been established. That is that the % R before the sharp rise to the T.O. of the weak oscillator must be greater than the

FIG.2.7a



FIG. 2.7b



FIG.2.8



% R after the tail over from the L.O. of the strong oscillator - as shown.

 ΔR here has been exaggerated to show the concept involved, but in real terms values of $\Delta R \approx 3\%$ are common. Similar results have been deduced previously (Gardner 1974).

All the above guide lines have been deduced empirically with no theoretical justification. If applied carefully, taking note of the cautions mentioned herein, the % R curve can be adjusted to give positive values of k (and hence ε ") with no noticeable distortion to the results obtained, T.O. frequencies being monitored with those obtained from i.r. mulls.

As a final note, cases do occur with multi-oscillator problems, i.e. 9-10 oscillators in each orientation, when no amount of subtle correction will yield positive values of k. Unfortunately such cases do not have an easy solution. θ is calculated over all values of R over all wavelengths and hence distortions to θ can be cumulative. In the absence of more empirical data, guide lines for such circumstances cannot be given.

Listings of all programs are given in appendices 1-3.

Appendix 1

Kramers-Kronig analysis program : optical constants calculated directly from input data.

Appendix 2

Simple harmonic oscillator program : optical constants calculated from a synthetically generated spectrum, using initial guesses for a) transverse optic mode frequency, b) transverse optic damping term, c) oscillator strength.

Appendix 3

Simple harmonic oscillator program : optical constants calculated from a synthetically generated spectrum, using initial guesses for a) transverse optic mode frequency, b) transverse optic damping term, c) longitudinal optic mode frequency, d) longitudinal optic damping term.

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Section B

The Raman Process, Crystal Growth

The Raman Effect

In the Raman effect an incident photon interacts with the crystal with the creation or destruction of a phonon to produce a scattered photon of a new frequency. This is inelastic light scattering.

The total energy, and hence wave vector, is conserved in the process

$$k_i = k_s + k_p$$

:, k_s and k_p represent the wave vectors of the incident and scattered photons and the phonon respectively. As k is related to w (frequency) as in Chapter one:

$$w_s = w_i \pm w_p$$

The difference between the frequencies of the incident and scattered photons is the phonon frequency.

The process can result in the scattered photon having greater or lesser energy than the incident photon. The former is described as the anti-Stokes effect and the latter as the Stokes effect.

It is seen practically that the Stokes effect results in a more intense spectrum. This is because in the anti-Stokes process a phonon is destroyed and involves the medium in a vibrationally excited state. Therefore the intensity will be related to the Boltzmann energy distribution for that state. Gilson and Hendra (1970) have reviewed the Raman process and a detailed account is given. The following is a representation of the facts relevant to this thesis.

The detailed mechanism of the Raman process is still not fully understood. However the essential theory relevant to its use has been well documented. The Raman process can be explained by the introduction of an induced dipole moment in an electron cloud by the oscillating electric vector of the incident radiation. Vibrations are observed if there is a change in the polarisability of the electron cloud due to the displacements of the nuclei involved.

The assumption is made that the energy of the incident radiation is insufficient to promote the system to an electronic excited state. This is valid even in the case of modern lasers which are used as the source of incident radiation.

It may be imagined that a transient intermediate electronic state between the ground and first excited electronic states is created by the absorption of photons by the medium. A photon is then emitted which allows the medium to return to the ground electronic state, but in a higher vibrational level. The result

is that the phonon produced is equivalent to a simple vibrational transition. No order is placed on the vibrational level which the medium returns to, this is determined by a term known as the "probability of transition" a description of which will not be attempted here. A review of the process has been given by Peticolas (1972).

Placzek (1962) describes the theory of the effect in classical terms using the polarisability of the medium (α) in relation to a normal coordinate (q).

Placzek has shown that Raman intensity is proportional $(\frac{\partial \alpha}{\partial q})^2$

and has shown that this has the form of a second rank tensor.

$$\begin{pmatrix} \frac{\partial \alpha}{\partial q} \end{pmatrix}_{i} \equiv \alpha' = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{zz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix}$$

to

x, y and z are the orthogonal axes. The tensor α_{xy} denotes the magnitude of the x component of the dipole moment, induced by the y component of the oscillating electric field.

Placzek has also shown that the relation:

$$\left(\frac{\partial \alpha}{\partial q}\right)^2 \alpha(\text{proportional})\mu_{um}^2$$

 μ_{im} is the transition moment such that:

$$\mu_{um} = \Psi_{u} \alpha' \Psi_{m}^{2} \tau$$

 Ψ_u and Ψ_m are the eigen states of the initial and final vibrational levels. However it has been shown that

 $\mu_{um} \ge 0$ if and only if $\Psi_{u} \alpha' \Psi_{m}$ contains the totally symmetric representation A_{1g} . The representation for a product r_{um} will only contain A_{1g} if $\Gamma_{u} = \Gamma_{m}$. Since Ψ_{u} must be totally symmetry (as it is the ground state) the product $\alpha' \Psi_{m}$ must contain A_{1g} .

Thus the final vibrational state will have the same representation as the polarisability tensor if it is Raman active. The species of a polarisability tensor is obtained from the point group table corresponding to the factor group of the crystal.

The nomenclature α_{xy} indicates that if the incident photon is polarised with respect to x, the scattered photon will be polarised with respect to y. Therefore it is possible to assign symmetry species of a Raman spectrum using polarised radiation and a polariser incorporated into the analyser for the scattered light.

The notation of Porto <u>et al</u> (1966) is used by single crystal spectroscopists therefore x(zx)y represents an incident beam

parallel to the x axis of a crystal polarised with respect to the z axis, and scattered photons parallel to the y crystal axis polarised with respect to the x axis.

If a solid is examined by Raman spectroscopy and the unit cell does not possess a centre of inversion, it is possible in certain orientations to observe the phenonmenon of L.O. T.O. splitting.

Splitting of Longitudinal and Transverse Optic Modes

I.r. active modes have been discussed in section A; it was established that the frequencies of T.O. and L.O. modes differ. The magnitude of the difference depends on the material under investigation. Strongly ionic materials may have a T.O.-L.O. split of $\sim 100 \text{ cm}^{-1}$. "Molecular" materials may exhibit a very small splitting.

The existence of both T.O. and L.O. modes for a symmetry species may be predicted using a vector diagram, (see figure 2.9). If the phonon propagation direction is in the plane of the directions of both incident and scattered photons, and the phonon polarisation direction is also in this plane, both L.O. and T.O. may be active, if the species is both i.r. and Raman active.

If the polarisations of both incident and scattered photons are parallel to crystallographic axes in high symmetry species several simplifications can be made. If these conditions are not

FIG. 2.9



observed, it is possible to observe "hybrid" L.O. and T.O. modes, a description of which will not be attempted here but has been discussed by Wilkinson et al (1971).

If the example of D_3 symmetry is taken, operations of type E are both i.r. and Raman active, the tensor components describing phonon polarisation are given by:

For a 90° Raman scattering experiment using the orientations x(yx)y and x(zx)y the phonon polarisation is y. In the case of x(yz)y the phonon polarisation is x. In all three cases the phonon polarisation is the x-y plane, and L.O. and T.O. modes may appear. Where splitting is small a band of intermediate frequency may be observed.

Growth of Crystals

Unless otherwise stated in the text, all crystals were grown by slow evaporation of solutions, the precise conditions being given in the relevant chapters. In the case of the mercuric halides $HgCl_2$, $HgBr_2$ these were grown by vapour phase deposition. The apparatus shown in figure 2.10 was mounted inside the oven shown in figure 2.11. The glass tubes were packed with purified compound and sealed by forming a constriction at the end of the tube and fusing a glass rod onto the constriction. The thin wire placed in the capillary was then removed and the apparatus was evacuated by attaching a rubber tube onto the open end and fitted with a tap. A plug of sublimed compound collected in the wide bore of the tube and sealed the apparatus during extrusion.

The apparatus was pulled through a temperature gradient in the oven by means of a sliding rail attached to rotating discs by wire. The discs were fitted with grooves of varying diameter so that the rate of extrusion could be varied. The average rate of pulling consistent with crystals of good optical quality was not greater than 1 cm per day.

Examination of Crystals

The crystals obtained by either of the two methods described above were frequently different sizes and often showed incomplete development of faces, the face which was in contact with the vessel would be poorly developed. The other faces exposed to either the saturated solution or the vapour of the compound showed a high





degree of development. If a crystal of a size suitable for spectroscopic work (<u>ca</u>. 5 mm x 3 mm x 2 mm) was selected on the basis of a well developed set of faces the "optical quality" could be determined using the polarising microscope. As well as locating crystallographic axes this method enables the distinction between twinned and untwinned crystals. Twinned crystals rarely grow in exactly parallel directions, and thus the presence of a twin is distinguished by incomplete extinction. A series of "growth **rings**" caused by the intermittant and rapid deposition of material can also be distinguished; these are characterised by small bright spots in the crystal while under extinction. The quality of results obtained is directly linked to the quality of the crystal and thus crystals should be selected showing the highest possible optical quality.

Raman and I.R. Experiments

The layout of the reflectance unit used on the Beckmann RIIC FS720 interferrometer has already been shown (figure 2.1. section A). The principle of operation of this machine has been described by Martin (1966). Some data was also collected using a Perkin-Elmer PE225 grating spectrometer.

Polarised i.r. information was collected using the following polarisers in the frequency ranges shown.

FS720

$0-600 \text{ cm}^{-1}$	Perkin-Elmer gold wire grid mounted onto	
	polyethylene	
600-1000 cm ⁻¹	KRS5 polariser made by Oxford instruments	
PE225		
$200-2000 \text{ cm}^{-1}$	Perkin-Elmer gold wire grid mounted onto	

silver bromide

Because of the mode of operation of the FS720 it is necessary to use filters for the radiation which cut-off the high frequency (unwanted) part of the radiation. Suitable filters for each of the beam-splitter ranges of the FS720 are:

Range	Beam Splitter	Filter
10- 110 cm	⁻¹ 25 μ M	Teflon
	(100 G)	Polyothylong field
20- 200 cm ⁻¹	-1 12 µ M	Teflon lens used
	(50 G)	
40- 400 cm ⁻¹	-1 6μΜ	None
	(25 G)	•
200- 600 cm	-1 3.6 μ M	Beckmann No.9
	(15 G)	low pass filter
600-1000 cm	-1 6μP	Grubb-Parsons
		low pass filter

G refers to the "gauge" of the Melinex (M) (polyethylene terephthalate), P refers to polypropylene.

The three low frequency ranges are examined using a polythene field lens, this shows very strong absorptions above <u>ca</u>. 500 cm^{-1} and hence no filter is necessary for the range 40-400 cm⁻¹.

A computer program is described elsewhere by Appleby (1977) for computing the results obtained from the FS720.

The PE225 was found to have several drawbacks; the major one being the thermal energy available from the beam. Low temperature work was extremely difficult and some crystals showed a small amount of sublimation or decomposition whilst under examination.

The Raman instrument used in this study is a Coderg T800 triple-monochromator machire. This has four independent slits and two photo-multipliers, one for use at the "blue" end of the visible spectrum, the other for use at the "red" end of the spectrum. The optical layout of this machine has been discussed by Trumble (1974).

Most of the information was collected using a Coherent Radiation Laboratories model 52A argon-ion laser which has two powerful emission lines. 4880 Å (488 nm) "blue line" and 5145 Å (514.5 nm) "green line".

The optical layout for 90°, 180° and 0° scattering experiments is shown in figure 2.12. The polarisation of the incident beam is





0° Scattering

varied by the use of a $\lambda/2$ plate, this rotates the plane of polarisation of the laser. The analyser enables selection of scattered radiation with respect to crystallographic axes. The $\lambda/4$ plate effectively "scrambles" the polarisation of the beam of scattered photons to safeguard that the sensitivity of the detection system does not vary with light polarisation.

Preparation of Samples

As discussed in section A, transmission samples must be very thin indeed. A face is selected containing the axes required, or a face is cut containing the axes, this is then mounted directly onto a plate of material transparent to the radiation in the frequency range required. Alternatively, the face may be mounted onto a disc of type shown in figure 2.13(a), the disc is made of brass or copper, different frequency ranges may therefore be studied with the same mount. The conical section acts as a condenser of radiation, "thick" samples may be studied if they are not strongly absorbing.

Figure 2.13(b) shows the arrangement of mounting for reflection measurements. Crystals are polished with a soft cloth to remove any grease or dirt placed on them during handling. The area surrounding the crystal was "masked" using black paper, this is to stop stray reflection from the copper disc. Trial experiments were conducted to deduce the best masking material. Copper
FIG. 2.13a



FIG. 2.13b



FIG. 2.13c



painted with matt black paint was tried, along with black rubber and various other materials. The conclusion was that black paper was far superior to any other material.

Crystals for Raman experiments were mounted onto copper posts as shown in figure 2.13(c). Epoxy resin into which aluminium powder had been mixed was used. The posts were made so that they would easily fit into the cryostat used.

Cryostats Used

Much of the low temperature work for this thesis was collected using a Cryogenic Technology C.T.I. model 20 closed-circuit liquid helium cryostat. This was fitted with a temperature controller which theoretically allowed any temperature between $300-10^{\circ}$ K to be obtained and maintained. It was discovered early in this program of research that temperatures in the order of $< 100^{\circ}$ K were not being obtained. A cold shield was designed for the purposes of this thesis which was mounted onto the nominal 77° K first stage cooling unit of the C.T.I. The cooling block was then surrounded by a copper band at 77° K during cooling, although this added to the load to be cooled, the radiation losses were drastically cut. Temperatures in the order of 30° K could be obtained subsequently. At all stages temperatures were monitored using a thermocouple.

Some data was also collected using a "home-made" liquid nitrogen cryostat with which temperatures of 115⁰K could be obtained.

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Chapter Three

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Vibrational Spectra of Topaz, and Some Data for Spodumene

Introduction

Both topaz and spodumene are minerals. Problems are frequently encountered in the vibrational studies of minerals, because by definition their compositions may vary within certain set limits. A "solid solution" series may be formed where the variable element may be present in a concentration of 0-100% of that allowed.

It can be reasonably expected that the two so-called "end-members" of a series (those which contain respectively 0% and 100% of the variable element) will show significant differences in their vibrational spectra. In addition, the disordering which occurs due to the presence of variable amounts of an element (different sized ions may well distort the lattice symmetry) will be reflected in the quality of the spectra obtained. Mineral spectra very seldom show any appreciable change on cooling to low temperatures. Therefore resolution of small features, or broad bands is frequently impossible.

Interpretation of mineral spectra and any assignments made can only be tentative, except in the case of well defined and separated regions of the spectra, or if confirmation is available by alternative means such as normal coordinate analysis (N.C.A.).

Although much information about the i.r. spectra of silicate minerals is available, and to a lesser extent their Raman spectra; reviews are given by Farmer (1974), Lazarev (1962), and Karr (1975), very little work has been done using oriented samples in polarised light. Such studies are essential prerequisites to a full understanding of what are often very complex spectra, since silicate minerals commonly have large unit cells of low symmetry.

Single-crystal data collected for beryl (Adams and Gardner 1975) and benitoite (Adams and Gardner 1976) are examples of how an understanding of the structures, coupled with oriented aralysis by selection rules, can lead to an understanding of the construction of the spectra, thus making a partial or full assignment possible.

Theory (Topaz)

The X-ray study of topaz $Al_2(OH,F)_2SiO_4$ by Wyckoff (1968) has established the symmetry as Pnma (D_{2h}^{16}) with z = 4. It is therefore a primitive unit cell of orthorhombic symmetry with four molecules per unit cell.

The silicon atom and half the oxygen atoms occupy C_{S} sites with all other atoms on general sites. The factor group analysis is shown in Table 3.1.

Topaz is classified as an orthosilicate and contains discrete $(SiO_4)^{4^-}$ ions, therefore information concerning the Si-O modes may be inferred in the absence of Si-O-Si modes.

Adams (1974) has discussed bond directionality and bond character, however the decomposition into internal and external modes should not be taken to infer anything quantitative about the bond character, even though the Si-O-Al bond may be presumed to be very directional.

The Al atom is in octahedral coordination to oxygen from four separate silicate groups, the remaining two positions being occupied by either oxygen from OH groups or F. Porto and Krishnan (1967) have reported optically active T.O. phonons as high as 751 cm⁻¹ for α -Al₂O₃ where Al is in a distorted octahedral environment, similar high frequencies for topaz Al-O may therefore be expected.

Experimental

The sample of topaz used to collect data was of side <u>ca</u>. $1 \times 1 \times 1 \text{ cm}^3$ and was cut from a colourless block of excellent optical quality. Kostov (1968) has reported that topaz commonly exhibits a cleavage parallel to the (001) faces. This appeared to be the case with our specimen, which on examination under a polarising microscope revealed two orthogonal indicatrix directions in the plane of the original block.

The sample was cut from the block, which was mounted in a goniometer, along these directions using a diamond impregnated saw. The freshly cut piece was then polished, first with boron carbide grit 1000 and then with alumina. A preliminary study of the single crystal Raman data obtained, revealed significant departures from F.G.A. predictions and indicated an incorrect choice of axes. A Weissenberg photograph of a small chip of the sample clearly showed that in terms of the axis set given by Wychoff, the cleavage plane of the original block was parallel to (010). The indicatrix axes taken were therefore: $x = a_0$ (4.6499), $Y = b_0$ (8.7968), $Z = c_0$ (8.3909), cell parameters being in parentheses.

Results and Discussion

The results obtained are shown in figures 3.1, 3.2a and 3.2b and summarised in Tables 3.2 and 3.3. The presence of hydroxyl is clearly demonstrated by the Raman bands at 1166 cm⁻¹ δ (OH) and 3655 ν (OH).

The only reliable guide is the representation of optically allowed modes, which is:

 $N_{opt} = 15A_g + 12B_{1g} + 15B_{2g} + 12B_{3g} + 14B_{1u} + 11B_{2u} + 14B_{3u}$

Single crystal i.r. reflectance data and Raman data have been collected by Serroin and Piriou (1973) and Hohler and Fünck (1973) for forsterite (Mg_2SiO_4) which is also an orthosilicate. On the basis of this data an N.C.A. analysis has been made by Devarajan and Fünck (1975).

The bonding between Mg^{2+} and $(SiO_4)^{4-}$ is weaker than that between Al^{3+} and $(SiO_4)^{4-}$ and results in a region of no absorption in the spectra between <u>ca</u>. 600-800 cm⁻¹. This allows the v(Si-0) region to be treated separately, as these modes are expected to occur >800 cm⁻¹. However, none of the authors have concluded a fully consistent interpretation of all the data.

The region below 600 cm⁻¹ will contain the v_2 and v_4 modes of the $(SiO_4)^{4-}$ anion, this region is also characterised by lattice modes and the two sets become significantly mixed. An assignment in this region can only be tentative.

The Raman data reported here for topaz shows a much smaller gap in the region below v(Si-0), the i.r. data shows only one very weak peak in this region. Bands in the frequency range 600-800 cm⁻¹ must be considered good candidates for v(Al-0) where the oxygen is from $(SiO_4)^{4-}$.

The v(SiO) as ignment (>800 cm⁻¹)

Figure 3.4 shows the modes of vibration of the isolated $(SiO_4)^{4^-}$ ion. The correlation table incorporated into Table 3.1 shows how these modes will become mixed in the spectrum of the crystal.

Species A_g and B_{2g} contain identical representations for

$v_1 + v_2 + 2v_3 + 2v_4$

Figures 3.2 and 3.3 show that in A_g and B_{2g} spectra, one band is present at significantly lower energy than the other two in these species, implying that $v_1 < v_3$. The bands in the B_{1g} and B_{3g} spectra at 1006 and 984 cm⁻¹ respectively can only originate from v_3 , and are significantly higher in frequency than the lower bands in A_g and B_{2g} attributed to v_1 .

A single mode is predicted in B_{2u} originating from v_3 . Figure 3.1 shows a very broad region of reflectance, corresponding to a very intense absorption, with a T.O. frequency of 870 cm⁻¹. Since this is the dominant feature it is regarded as the fundamental, the weak feature at <u>ca</u>. 1000 cm⁻¹ is attributed to a two-phonon mode.

It is not uncommon to observe two-phonon modes in i.r. reflectance spectra - not only of minerals. These must be distinguished before an assignment can be made. On present evidence there is no <u>a priori</u> means of making such a distinction, unless a thermal dependence study is done in order to evaluate cubic and quartic anharmonicity. The guide here is internal consistency (backed up by Raman data) and the intuitive experience gained in reflectance spectroscopy.

In the B_{1u} spectrum 3 modes are predicted $v_1 + 2v_3$. Three bands are found, these are regarded as fundamentals.

In the B_{3u} spectrum 3 modes are predicted $v_1 + 2v_3$. Three bands are found, and are also regarded as fundamentals.

The following assignment has been deduced for the ν (Si-O) region.



The assignment for v_1 shows a high consistency and a range of 54 cm⁻¹. The assignment for v_3 A' components yields a splitting of 70 cm⁻¹ which is regarded as reasonable. The A" assignment is less satisfactory, at first sight a splitting of 136 cm⁻¹ seems rather large. If the weak feature in B_{2u} at <u>ca</u>. 1000 cm⁻¹ was chosen the splitting would have been very small, perhaps too small.

It is regarded that the v(Si-0) assignment is established. It is interesting to note that the N.C.A. of forsterite by Devarjan and Funck presented a similar problem. The final assign-

ment gave v_3 a range of <u>ca</u>. 130 cm⁻¹ and v_1 a range of 16 cm⁻¹.

The region below v(Si-0)

It is impossible to establish a unique assignment for this region in the absence of a full N.C.A. treatment. The v_2 and v_4 modes of $(SiO_4)^{4-}$ are mixed with the lattice modes. Comparison of topaz with other orthosilicates suggests that none of the v_2 and v_4 components occur above <u>ca</u>. 650 cm⁻¹. Accordingly the very weak i.r. feature at <u>ca</u>. 760 cm⁻¹ and Raman bands at 682, 706 and 843 cm⁻¹ can be regarded as either due to Al-O (Si) bond stretching or to two phonon processes. The fundamentals v(Al-OH) and v(Al-F) are most probably in the region below 650 cm⁻¹.

The region below 400 cm^{-1} to the Raman band at 155 cm^{-1} and i.r. bands down to 175 cm^{-1} are most probably lattice modes. The absence of bands below 155 cm^{-1} is consistent with a structure in which only light atoms are involved.

It is useful only to note the number of modes predicted with those found.

	Ag	B _{lg}	B _{2g}	B _{3g}	B _{lu}	B _{2u}	B _{3u}
F.g.a.	12	11	12	11	11	10	11
observed	11	10	7	10	11	9	10

Since the completion of this work an F.G.A. of topaz has been published by Kovaleva (1975). I.r. reflectance data is reported in the region 1200-400 cm⁻¹. Kovaleva reports only reflectance maxima and not T.O. positions, so direct comparison cannot be made. A large degree of agreement is seen between spectra, Kovaleva reported a secondary feature on the highest v_3 (Si-O) band in B_{1u} which is not regarded as a fundamental here. There is an inconsistency between the labelling of spectra, compatible spectra are found by interchanging Kovaleva's species of B_{1u} and B_{2u} to fit those reported here. This would seem to indicate an incorrect choice of axes, which is interesting in view of the knowledge gained from preliminary Raman experiments reported here. In view of the Raman data and low frequency i.r. reported here, it is believed that this assignment is the correct one (Adams and Hills 1977). Minor deviations in reflectance band shapes etc., are likely to be due to the differing amounts of OH and F in our respective crystals.

Theory (Spodumene)

The X-ray study of Spodumene (LiAlSi₂O₆) by Wyckoff (1968) has determined the symmetry as $C2/C \equiv C_{2h}^{6}$ with z = 2. It is therefore a unit cell of monoclinic symmetry with two molecules in the primitive cell.

Spodumene is classified as a Pyroxene and contains chains of Si_2O_6 units parallel to the <u>c</u>-axis.

Clarck <u>et al</u> (1969) have shown that there is a small distortion of the atom positions which indicates $C2 \equiv C_2^3$ symmetry, but conclude that the distortion is sufficiently small to enable C2/C to be safely used.

Gervais, Piriou and Cabannes (1973) have studied the thermal dependence of the A_u modes of spodumene, but report no data for the B_u modes. A_u was determined as: 295, 314.7, 342, 449, 486.7, 494, 526.5, 571, 856.5, 993, 1068, 1088, and 1130.5 cm⁻¹, the bands between and including 342-494 cm⁻¹ being assigned to v_2 and v_4 components of the $(Si_2O_6)^{4-}$ ion.

Factor group analysis predicts for the optic branch

 $N_{opt} = 14A_g + 16B_g + 13A_u + 14B_u$

Results and Discussion

Raman data was collected on the crystal which had a small face ground parallel to the <u>c</u>-axis using boron carbide grit 1000. Unfortunately the crystal showed no significant intensity changes with orientation using all available scattering geometries (90° , 180° , 0° scatter). In addition, strong fluorescence was observed which remained even on the changing of exciting line used. Using 488 nm radiation the following bands were observed above noise level: 134, 190, 254, 300, 360(m), 397, 446, 523, 590, 712(v.s.), 1076 cm⁻¹, all weak unless otherwise indicated. Of the $14A_g$ and $16B_g$ modes predicted v(Si-0) accounts for $3A_g + 3B_g$. Only one band at 1076 cm⁻¹ was observed for this region. Using i.r. reflectance the following bands were located:

 $A_u(E_\parallel C)$ 229, 270, 444, <u>ca.500</u>, 1008, <u>ca.1050</u> cm⁻¹ $B_u(E_\perp C)$ 325, 358, 392, 463, 619, <u>ca.650</u>, 890, 1085, 1205 cm⁻¹.

The agreement with Gervais <u>et al</u> for the A_u modes seems to be weak except in the cases of the bands at 444, <u>ca.500</u>, 1008 and 1050 cm⁻¹ reported here, and may well be due to the poor sample used. This is shown by the lack of orientation effects in the Raman.

F.g.a. predicts of $v(\text{Si-O}) 3A_u + 3B_u$, the B_u spectrum may be viewed sceptically, however 3 bands may be assigned for v(Si-O) at 1085, 890, and <u>ca.650</u> cm⁻¹. Bands occurring above 1100 cm⁻¹ are correlated with Si-O-Si bridges.

Further discussion is of little use in the absence of a better specimen.

for topaz.

<u>D₂h</u>	$N_{T}^{\underline{a}}$	т _А	Т	R	N vib	ν(Si-0)	Activities
Ag	15		8	l	6	3	x^2 , y^2 , z^2
^B lg	12		7	2	3	l	ху
^B 2g	15		8	l	6	3	xz
B _{3g}	12		7	2	3	l	yz
A _u	12		7	2	3	l	
^B lu	15	1	7	l	6	3	z
^B 2u	12	1	6	2	3	1	У
^B 3u	15	1	7	1	6	3	X

A : Factor group analysis

B : Correlation scheme

<u>Ion</u> , <u>T_d</u>	Site, $\underline{c_s}$ (xz)		<u>Crystal</u> , <u>D</u> 2 <u>h</u>
$v_1 a_1$	A'	6A' _×4 →	$6(A_g + B_{2g} + B_{1u} + B_{3u})$
ν ₂ e	A' + A" }		
v3, v4t2	2A' + A"	за" →	$3(B_{1g} + B_{3g} + A_{u} + B_{2u})$

 $\frac{a}{T} = N_{T}$ = total number of unit cell modes; T_{A} = acoustic, T = optic branch modes; R = rotatory modes of $(SiO_{4})^{4-}$; N_{vib} = internal modes of $(SiO_{4})^{4-}$ of which $\nu(Si-O)$ forms part. Table 3.2 I.r. wavenumbers/cm⁻¹ for single-crystal topaz.

	B _{3u} (x)	B _{2u} (y)	B _{lu} (z)
		178w	175w
	208w		
	268vs	29lvs	292w
	309vs		310w
		335 vs	336w
	389vs	364m	375ms
	419ms		420w
	463ms	450ms	444vs
	489vs	473w	489vs
		520ms	513vs
	544wm	545s	
	572w		
	610vs	6llvs	609vs
			∿760vw
ν1	857s		875w
ν(Si-0)	936vs	870ms	895vs
$\left[\frac{b}{b}\right]^{3}$	<u>ca</u> .985sh	995vw <u>a</u>	995vs

- <u>a</u> Not a fundamental.
- $\underline{\mathbb{L}}$ This region is complicated and appears to contain a further oscillator.

	unit	ts) a for	topaz.				
v/cm ⁻¹	Symmetry species	z(xx)y	z(yy)x	y(zz)x	z(yx)y	z(xz)x	z(yz)y
155	Ag	6	25	24			
165	Big				68		
171	B _{3g}						6
191	B _{3g}						8
237	B _{2g}					100	
242	Ag	49	100	100	16		15
266	B _{2g}					37	
270	Ag	100	100	100	22		20
273	B _{2g}					40	
288	A_g/B_{1g}	100	100	90	53	14	
292	B _{3g}						20
315	Blg				68		10
334	Ag	81	8	38	15	4	
351	B _{3g}						6
360	B _{2g}					48	
369	B _{1g}				20		
373	B _{3g}						33
380	B _{2g}					15	
402	B _{1g}				8		
405	Ag	39	14	16			
424	Blg				18		
441	B _{3g}						10
460	Ag	62	6		8	6	
474	B _{3g}						10
482	B _{3g}						27
491	Ag		6	8			
495	B ₂ g					17	
499	Blg				8		
509	B _{1g}				22		
521	A		2	66			
549	B ₂					35	
561	Ag Ag	1	19	19			
599	Bla				10		

Raman wavenumbers/ cm^{-1} and intensities (arbitrary

Table 3.3

86.

/contd...

Table 3.3 (contd.)

	v/cm ⁻¹	Symmetry species	z(xx)y	z(yy)x	y(zz)x	z(yx)y	z(xz)x	z(yz)y
	641	Bag						10
	646	Ag	2	З				
	682	B _{3g}						6
	706	Blg				16		
	843	B _{2g}					4	
ν, ∫	854	Ag	40	1	4	10	6	
	908	B _{2g}					32	
ſ	926	Ag/B2g	50		88	12	36	
	938	Ag		64				
V3 {	984	B _{3g}						100
	1006	Blg				42		
l	1008	B ₂ g					35	
δ(OH)	1166	Ag/Blg/B3g	14			20		10
ν(OH)	3655	Ag		10				

a (xx)y, (yy), and (zz) spectra recorded at 0.5 cm⁻¹ spectral slit width; (xy), (yz), and (zx) spectra recorded at 3.25 cm⁻¹ spectral slit width. The intensities in the two sets cannot be compared directly.

















FIG. 3.4



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Chapter Four

Vibrational Spectra of Aluminium Trichloride Hexahydrate

Introduction

Although much information has been collected on the vibrational motions of the water molecule coordinated to metal ions (reviews are given by Adams, 1967 and Brun 1968), the data is still not satisfactorily understood. Relatively little Raman and fari.r. data has been published on hydrated metal ions in the solid state; the majority of data has been collected in the 250-4000 cm^{-1} i.r. region, and few data sets contain symmetry information.

The principal experimental evidence given in support of assignments is based upon the frequency changes on deuteriation. The skeletal modes of the molecules, due to metal-oxygen stretches and deformations, are expected to show some sensitivity on deuteriation, the "effective mass" of the ligand being increased from 18 to 20. The external modes of the molecules (translations and rotations) are sensitive only to changes in moments of inertia, and show very small changes due to the extra mass of the deuterium atoms. The modes of the coordinated water molecules, "librations", i.e. restricted rotations and translations may be expected to show large shifts close to the theoretical $V_{\rm H}/v_{\rm p} = \frac{1}{f_2}$.

The assignment of the modes due to water motions has been the subject of great debate. Normal coordinate analysis calculations, such as those of Nakagawa and Shimanouchi (1964), have been published for hydrate complexes $[M(OH_2)_n]^{2+}$ n = 4, 6; these may be unreliable in the absence of a unique assignment, because of the large number of modes which can occur. A strict examination of the substantial evidence for hydrate complexes (hexahydrates in particular) show that they are less well-understood than the complex spectra of the many phases of ice.

The approach adopted for this study is the consistency of the evidence accumulated. The isolated water molecule has C_{2v} symmetry, on coordination to a cation the three rotational and the three translational degrees of freedom of the isolated molecule are incorporated into those of the complex, a description is given by Adams and Lock (1971). For a single coordinated water molecule six modes will occur, these are: a V(M-OH₂) mode; two skeletal modes involving a deformation of the M-O bond; and three "librational" modes, these are described by $\rho_{\rm p}$ (a rocking mode), $\rho_{\rm T}$ (a twisting mode) and $\rho_{\rm W}$ (a "wagging" mode). The three forms are shown below.



It is the energy order of these three modes which is often at the centre of the controversy of the assignment in hydrates. It

can be inferred from mono-hydrated anions such as $[FeCl_5(OH_2)]^{2-}$ that the order $\rho_W > \rho_r$ is usually obeyed. This is reasonable when the relative moments of inertia associated with the rotational motions of water are compared. Calculated values for the moments of inertia of the rotational motions which become ρ_W , ρ_t and ρ_r in the coordinated complex are in the ratio 1:1.9:2.9 in the free molecule. Evidence accumulated by Adams and Lock (1971) and Shankel and Bates (1976) would indicate that $\rho_W > \rho_r$, in mono and di-aquated complexes, is the energy order found. The place of ρ_t has not yet been settled, this is because it is likely to be weak in i.r. spectra. This mode originates as the rotation about (z) in the free molecule, and has symmetry A_2 in the point group C_{2v} , and is not i.r. active. It may gain activity in the complex by virtue of the symmetry subtended by the rest of the complex (see Chapter one).

Hexahydrate complexes have received attention recently, reports are in the literature on the $[Ni(OH_2)_6]^{2+}$ ion in the compounds $[Ni(OH_2)_6][SnCl_6]$ by Jäger and Schaack (1973) and Adams and Trumble (1974) and also $[Ni(OH_2)_6]SO_4$ by Jäger and Schaack (1973) and Jani <u>et al</u> (1974). Partial Raman studies of $[Mg(OH_2)_6]$ - $SO_4.H_2O$ by Hillaire <u>et al</u> (A) (1971) and $[Mg(OH_2)_6][PH_2O_2]$ by Hillaire <u>et al</u> (B) (1971) provide a good basis for a survey of the relative magnitudes of the modes predicted. The overall order of $\rho_W > \rho_T > V(M-OH_2)$ has been accepted by all these authors and as such it seems very reasonable. Jäger and Schaack (1973) attributed bands at 290, 357 and 365 in the complex $[Ni(OH_2)_6][SnCl_6]$ to ρ_t modes of the complex. These shifted to 236, 272 and 292 respectively on deuteriation, in all cases the bands were only observed at 15 K or below; this assignment cannot be regarded as well substantiated.

An inelastic neutron scattering study of several hydrates by Prask and Boutin (1966) reveals bands attributable to water motions in the range of 300-900 cm⁻¹. This is compatible with most studies both i.r. and Raman on a wide range of hydrates. Prask and Boutin obtained significantly different scattering spectra for AlCl₃.6H₂O and the isomorphous CrCl₃.6H₂O, this is attributed to the isomeric form of CrCl₃.6H₂O [Cr(OH₂)₅Cl]Cl₂.H₂O. Modes due to water motion are highly sensitive to metal oxidation state and hydrogen bonding and often show a large thermal dependence.

Three single-crystal Raman studies of AlCl₃.6H₂O have been reported previously. The studies of Galy (1953) and Weil-Marchand (1955) were confined to the internal modes of the coordinated water molecules. The third study by Champier and Galy (1954) studied the region up to 1000 cm⁻¹. The results reported here confirm the assignments of the stronger bands in most cases, but also reveal more detail. An i.r. study using the KBr pellet technique (Lucchesi and Glasson 1956) did not assign any symmetry labels to the sample, and the low frequency end was not observed.

Some interesting solution work by Mathieu (1950) and by da Silveira et al (1961, 1965) located v_1 , v_2 and v_5 using Raman spectroscopy on solutions of AlCl₃.

 v_1 was located at 525 cm⁻¹ on account of its polarised behaviour

 v_2 was located at 447 cm⁻¹ (depolarised)

 v_5 was located at 340 cm⁻¹

Experimental

Crystals of AlCl₃.6H₂O were grown by slow evaporation of aqueous solutions of AlCl₃ dissolved in 1:10 HCl:H₂O, the initial small precipitate of alumina was filtered off. The composition of the crystals was verified by thermogravimetric analysis. The crystals had well-developed faces of side <u>ca</u>. 10 x 5 x 2 mm³ and were of excellent optical quality. Extinction directions were found using a polarising microscope and are illustrated in figure 4.1. The deuteriate was prepared similarly using D₂O followed by two successive recrystallisations from D₂O.

It proved impossible to obtain sufficiently thin crystal sections for study by i.r. transmission because the material has a slight deliquescent nature and was mechanically unstable in thin sections. So the crystals were studied using reflectance spectroscopy using the method described in Chapter two, section B. Many attempts were made to obtain reflectance spectra at low temperatures, but were frustrated by a loss of reflectance on cooling. Attempts were also made to obtain spectra at >1000 cm⁻¹ using a grating spectrometer, but these failed due to partial dehydration of the crystals in the heat of the beam. Cooling these crystals in a cryostat to attempt to overcome this problem were frustrated by loss of reflectivity on cooling.

Samples were prepared for Raman work as in Chapter two, section B, excellent results were obtained. It proved impossible to achieve temperatures of below 115 K without the aid of the cold shield (see Chapter two, section B) which was designed after the completion of this work.

Theory

The symmetry of AlCl₃.6H₂O was determined by Andress and Carpenter (1934), it crystallises in the trigonal system with space group $R\overline{3}C \equiv D_{3d}^6$ with z = 2. A factor group analysis is shown in table 4.1(a) along with a correlation scheme for the internal modes of the AlO₆ octahedron in table 4.1(b). The bands of A and E symmetry should occur in close proximity as they would be degenerate if the complex had O_h symmetry. The overall symmetry of $[Al(OH_2)_6]^{3^+}$ is S₆ which requires that both components of the inactive v₆ mode are i.r. active. The Al-O bond distance was confirmed at 1.88 Å from a recent X-ray determination of $[A1(OH_2)_6][RuCl_6].4H_2O$ by Hopkins <u>et al</u> (1969).

The vibrational modes of a regular octahedron are shown in figure 4.2. The order of the skeletal modes follows from the dynamical equations:

$$v_1(A_{1g}) > v_2(E_g) > v_5(T_{2g})$$

 $v_3(T_{1u}) > v_4(T_{1u})$

in addition $v_5 \gtrsim \sqrt{2}v_6$ (from force constant relations) $v_6(T_{2u})$ The position of the v_3 relative to v_1 and v_2 (the other skeletal stretching modes) depends upon the magnitudes of the <u>GF</u> matrix elements, as described by Nakamoto (1963), and may be greater or less than v_1 , but is always greater than v_2 .

Results and Discussion

Some data which are useful for reference in this discussion are summarised in table 4.2. The data collected is for mono- and dihydrated complexes. The work on $Rb_2[NiCl_4(OH_2)_2]$ by Shankel and Bates (1976) is very useful as the crystal has a uni-molecular unit cell, so no coupling will be seen; also the data was recorded at very low temperatures. The fact that only two bands were found in both the i.r. and Raman spectra, which could be attributed to water "librations", indicates that ρ_t is weak and could well be absent from the spectra.

The Region Below 350 cm⁻¹

Results are shown in figures $4.3 \rightarrow 4.7$ and data are summarised in Table 4.3, 4.4(a), 4.4(b) and a comparison with some other hexahydrates is given in Table 4.5. Judging by values quoted for ρ_w , ρ_r and ρ_t , the only possible mode due to water motion in this region is ρ_t . All other modes in this region will be either internal modes of the AlO₆ group or lattice modes. None of the bands in this region shows a large deuteriation shift and therefore it is assigned as follows.

All lattice modes are translatory in type (see Table 4.1(a)). The two lowest energy Raman-active lattice modes, i.e. 71 (E_g) and 78 (A_{1g}) are considered as the predicted rotatory modes, and all others are assigned to translatory in type. This assumption is supported by the observation that there is very little sensitivity to deuteriation, the exception being the highest A_{1g} mode in this region which is reduced by exactly the amount calculated for a simple translation of the $[A1(OH_2)_6]^{3+}$ ion, 183 to 180 cm⁻¹.

The remaining bands are the v_4 , v_5 and v_6 components of the AlO₆ skeletal structure. Of these, only v_5 is allowed to have an A_{1g} component; the only reasonable assignment for it is 295 cm⁻¹, and it is accompanied by one of the required E_g components at 310 cm⁻¹, the other component is either degenerate or is absent.
The weighted average of these values places v_6 at 216 cm⁻¹ (using $v_5 = \sqrt{2}v_6$) this is very close to the average of the i.r. bands at 229 (A_{2u}) and 209 (E_u). The Kramers-Kronig analysis of the E_u spectrum of the protiate, and the values of T.O. frequencies estimated visually are in excellent agreement, except for the band at 209 cm⁻¹ which is significantly displaced from its estimated value. It is considered that this inconsistency is due to two modes of vibration which are <u>ca</u>. 10 cm⁻¹ apart, the width of the band could easily incorporate another mode in near coincidence. Accordingly the E_u v_6 modes are estimated to be 209 and 218 cm⁻¹. v_4 is present at 309 cm⁻¹ in A_{2u}, but no E_u component was found at ambient temperatures in either the protiate or the deuteriate, a weak band at 327 cm⁻¹ was observed in a mull of the protiate at liquid nitrogen temperatures, this is considered to be one of the missing E_u components.

All modes show deuteriation shifts as is required by the forms of their $\underline{\bigcirc}$ matrix elements, but these shifts are very much smaller than those of the modes due to water motion. v_5 for the deuteriate can be calculated using a crude model as

 $v_5' = v_5 ({}^{M}H_2 0/M_{D_2 0})^2$ taking masses of 18 and 20 respectively.

ν ₅	310	ν ₅ '	(calculated)	294	ν5 '	(observed)	291
	295	•		278			284

98.

 cm^{-1}

which shows a very reasonable agreement. Other modes can be calculated using the same model, and show a reasonable agreement; thus none of these modes are due to water librations, and are shown to be internal modes.

The Region Above 350 cm

This region contains all the librational modes of water, since ρ_t is shown to be absent < 350 cm⁻¹, in addition to ν_1 , ν_2 and ν_3 . Theory (Table 4.1) predicts that A_{1g} should contain four bands in this region, and four are observed. Similarly, E_g is predicted to contain eight bands, seven are actually observed. This is significant in that these bands must contain ρ_t , and place a lower limit of 524 cm⁻¹ on it (A_{1g} component).

All four A_{lg} bands in this region (524, 584, 701 and 800 cm⁻¹) are substantially shifted on deuteriation, but it is not immediately obvious which bands may be paired in the two spectra. The shift of v_1 on deuteriation may be calculated by a crude model as:

 $v_1' = v_1(M(H_2O)/M(D_2O))^{\frac{1}{2}}$

applied to each of the four A modes of the protiate we obtain

A _{lg} mode	v_1 ' (calc.)	A_{1g} mode (D ₂ O) obs.
524	497	418
584	554	504
701	665	593
800	759	650

Since the highest A_{1g} mode in the deuteriate is 650 cm⁻¹ it is obvious that the bond at 800 cm⁻¹ cannot be v_1 . Similarly the shift for the mode at 584 cm⁻¹ does not correspond sufficiently closely to any observed band in the deuteriate. Selecting v_1 as 524 cm⁻¹ or 701 cm⁻¹ the remaining bands may be paired:

 ν_1 (701) : 800 (593), 701 (650), 584 (504), 524 (418)

 v_1 (524) : 800 (650), 701 (593), 584 (418), 524 (504)

all of which yield reasonable deuteriation shifts.

Three arguments may be forwarded to resolve the position of v_1 . Firstly solution studies of AlCl₃ by Silveira <u>et al</u> (1961, 1965) concluded that v_1 was at 525 cm⁻¹, this is justified by the polarised behaviour of the mode. The other modes identified by Silveira <u>et al</u> were v_2 (447) and v_5 (340) cm⁻¹. Values for AlCl₃ in D₂O were v_1 (503), v_2 (433) and v_5 (313) cm⁻¹. All these values are very close to observed bands in solid AlCl₃.6H₂O and the deuteriate, and support v_1 at 524 cm⁻¹. The mode at 432 cm⁻¹ (Z_g) is assigned to v_2 which is in a reasonable position relative to v_5 . The remaining v_2 component may be either degenerate or of disappearingly weak intensity, v_2 may be seen to shift to 418 cm⁻¹ in the deuteriate which is a very reasonable shift.

The second line of argument is to perform a simple Normal Coordinate Analysis calculation. As v_2 and v_5 have been established, and only two possibilities exist for v_1 , it may be possible to compute values of v_3 and v_4 using these values and compare them with the observed results. The Urey-Bradley field was selected owing to the relative simplicity of the model. Three force constants are necessary to describe all of the modes of vibration of a regular octahedron using this model. These are:

K, metal-ligand stretching force constant
F, stretch-stretch interaction constant
H, angle bending constant

 $m dymes/A \times 10^{-5}$

Several assumptions are made. These include that each complex ion is isolated from the lattice, and that all the Al-O₆ skeletal modes are uneffected by removing the interactions associated with the lattice. Using the equation $|GF-E\lambda| = 0$ where G and F are G and F matrices respectively and E is the unit matrix. λ is related to observed frequencies by:

 $\lambda_{i}^{\frac{1}{2}} \times 1303.16 = w_{i}$ where w_{i} = observed frequency in cm⁻¹

The following relationships exist:

 A_{1g} v_1) $\mu_x(k + 4F) - \lambda_1 = 0$ E_g v_2) $\mu_x(k + 0.7F) - \lambda_2 = 0$

 $\mu_{\mathbf{X}}$ is the reduced mass of the ligand; k and F are force constants.

$$T_{2g}$$
 ν_5) $4\mu_x(H + 0.55F) - \lambda_5 = 0$
 T_{211} ν_6) $2\mu_x(H + 0.55F) - \lambda_6 = 0$

It can be seen clearly from these two equations that $v_5 = \sqrt{2}v_6$. H is the third force constant required for the analysis.

The $T_{\mbox{lu}}$ components ν_3 and ν_4 can be calculated using the equation:

$$\begin{vmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{vmatrix} \begin{vmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{vmatrix} - \begin{vmatrix} \lambda & 0 \\ 0 & \lambda \end{vmatrix} = 0$$

which simplifies to:

$$\lambda^2 - \lambda(G_{11}F_{11} + G_{22}F_{22} + 2G_{12}F_{12}) + \{(G_{11}G_{22} - G_{12})^2(F_{11}F_{22} - F_{12})^2\} = 0$$

This can be solved as a quadratic equation to find the coefficients, yielding values of λ for ν_3 and ν_4 .

$$G_{11} = (\mu_{x} + 2\mu_{m})$$

$$G_{12} = -\frac{4\mu_{m}}{r} = G_{21}$$

$$G_{22} = \frac{2}{r^{2}}(\mu_{x} + 4\mu_{m})$$

$$F_{11} = (k + 1.8F)$$

$$F_{12} = 0.9rF = F_{21}$$

$$F_{22} = r^{2}(H + 0.55F)$$

where $\mu_{\rm m}$ is the reduced mass of the metal atom, r is the metaloxygen bond distance. A simple computer program was written for the purposes of this thesis to calculate ν_3 and ν_4 from values fed in for ν_1 , ν_2 and ν_5 ; r was taken as 1.88Å following a recent Xray structure determination of $[Al(OH_2)_6][RuCl_6].4H_2O$ by Hopkins <u>et</u> al (1969). The results obtained were:

	$v_3(calc.)v_4(calc.)$	$v_4(obs.)$	k	F	Н
v _l (701)	591 269	309	1.22	0.92	-0.28
v ₁ (524)	653 319	309	1.79	0.26	0.09

With v_1 at 701 cm⁻¹ v_4 was calculated 40 cm⁻¹ below its observed value, in addition, the values of k and F are insufficiently different. F is much too large relative to k. With v_1 at 524 v_4 was calculated only 10 cm⁻¹ away from its observed value and k, F and H have reasonable magnitudes. This strongly supports v_1 at 524 cm⁻¹. A similar calculation for the deuteriate with v_1 at 504 cm⁻¹ gave v_3 at 644 cm⁻¹ and v_4 at 302 cm⁻¹ (observed in the deuteriate at 282 cm⁻¹). The exact positioning of v_3 with either of the above calculations has relative merits and disadvantages. The value of 591 cm⁻¹ for v_1 at 701 cm⁻¹ places v_3 near to the intense reflectance bands at 560 (A_{2u}) and 580 (E_u) which is reasonable since v_3 is reasonably expected to be a strongly allowed vibration in the i.r. However v_4 is much too low. The value of 653 with v_1 at 524 cm⁻¹ places v_3 near to the weak bands at 678 cm⁻¹ (A_{2u}) and 664 (E_u), it is not immediately obvious why v_3 should be so weak.

The third line of argument by which v_1 may be decided is that for each of the groups ρ_r , ρ_W , ρ_t there should be three bands bearing symmetry labels A, E, E. It is most useful here to consider the Raman data since the i.r. is obviously well short of the theoretically predicted number (this is considered in more detail later). How much splitting may be expected can be guessed from the behaviour of v(OH) and $\delta(OH)$. The A_{1g} components of v(OH)seen are the v_1 and v_3 modes of the H₂O molecule. E_g is missing two bands in this region. If the reasonable assumption is made that the two E_g modes observed are v_1 , the total Davydov splitting

is 31 cm⁻¹. Therefore equally modest splittings of the components of ρ_w , ρ_r and ρ_t should be observed. All components of $\nu(OH)$ are low in frequency compared to situations in which little or no hydrogen bonding is present, e.g. 3300 cm⁻¹ in the Raman spectrum of $[NiCl_4(OH_2)_2]^{2^-}$. If consideration of ν_3 is deferred, two alternative groupings of the modes may be postulated depending on the choice of ν_1 .



The i.r. assignment is the same in either case. The total Davydov splitting is rather large for the middle group whichever choice of v_1 is made.

If the i.r. data are now considered in detail, both $A_{2_{11}}$ and E_{u} spectra show reflectance bands at similar positions and of similar relative intensities. The A_{2u} spectrum shows three of the four predicted bands, the E_u spectrum shows only three of the theoretical eight bands. An explanation may be given in terms of the coupling between the molecules in the unit cell. If this is weak, as shown by the v_1 components of v(OH) the selection rules which apply are those of the site group S_6 . This describes the symmetry of the field which one complex ion experiences in the crystal, and correctly accounts for the absence of one v_5 (E_g) and one v_2 (E_g) component in the spectra. The coupling between molecules is via the weakly hydrogen bonded chlorides which separate the complex ions and therefore this explanation is plausible. Since A_{2g} is inactive, no further test of this theory can be made. The behaviour of ν_6 which according to S_6 symmetry should show only one $E_{\rm u}$ component is undecided. A .null spectrum at low temperature showed two components at ca. 210 cm⁻¹; the shape of the ε " function is indicative of two components in this region.

The groupings of the librational modes ρ_W , ρ_t and ρ_r is supported by the consideration of the moments of inertia of the isolated water molecule. For the free molecule, the motions which become ρ_W , ρ_t and ρ_r have moments of inertia in the ratio 1:1.9:2.9. The coordinated modes may therefore be reasonably presumed to follow the order $\rho_w > \rho_t > \rho_r$. There is good evidence that, at least for mono- and di-aquated complexes, $\rho_w > \rho_r$ (see Table 4.2), the position of ρ_t is unsettled. It is pro**posed** here that it lies between ρ_w and ρ_r , at least in hexa aquo complexes. The feebleness of the i.r. bands attributed to ρ_t is consistent with this assignment, since they arise from the inactive motion A_2 in C_{2_V} and are only made active by the field subtended by the surroundings.

The assignment of v_3 can no longer be neglected. Since evidence strongly follows v_1 at 524 cm⁻¹, v_3 must lie close to the region calculated for it, i.e. 653 cm^{-1} for the hydrate and 644 cm⁻¹ in the deuteriate. If v_1 is taken at 701 cm⁻¹ v_3 may lie beneath the very intense bands at 560 (A₂₁₁) and 580 (E₁). The assignment of these modes to $\rho_{\tt r}$ cannot be disturbed as both bands show very large shifts on deuteriation to ca. 400 cm^{-1} , yielding ratios of ~ 0.72 which is close to the expected 0.72 for librational modes. Unfortunately the i.r. reflectance spectra for the deuteriate in the region $>500 \text{ cm}^{-1}$ were of much lower quality than the protiate. It was not certain whether there were any weak bands at ca. 640 cm^{-1} which may be attributed to v_3 . Although it is not obvious why v_3 should be so weak, the bands at 678 $(A_{2_{11}})$ and 664 $(E_{1_{12}})$ are attributed to v_3 on the basis of evidence accumulated. This explains the absence of one A_{2u} mode, attributed to ρ_t , which is expected to be weak in the i.r.

The E_g spectrum of the deuteriate is difficult to explain unless some of the observed bands are attributed to more than one mode, since fewer bands are found than in the protiate. All these E_g bands are due to water librations since v_2 has been located at 423 and 418 cm⁻¹ in the hydrate and deuteriate respectively. On the basis of relative intensities the modes are paired as:

protiate	deuteriate	۷ 0 20/ _{۷H2} 0
534	408	0.78
563	443	0.78
610	504	0.83
825	617	0.75

These assignments are not entirely satisfactory. For a definitive assignment a much more detailed experimental approach must be adopted. Data should be collected for a range of temperatures over the i.r. and Raman region between $350-1000 \text{ cm}^{-1}$.

Conclusion

A comparison of the assignment here with those for other MO₆ skeletal modes for $[M(OH_2)_6]^{2^+}$ ions is given in Table 4.5. All frequencies appear to be considerably raised by the greater charge on aluminium, since the masses of aluminium and magnesium are not too dissimilar. For M = Ni there is a further reduction in $\nu_1,\,\nu_2$ and ν_3 frequencies due to the increased mass of the metal.

The spectrum of $[Al(OH_2)_6]Cl_3$ has been almost entirely established; there is some ambiguity about the positioning of v_3 . It is not clear why v_1 and v_3 should be so weak, as they should be very strongly allowed modes. Some further experimental work, on the deuteriate in particular, may allow a definitive assignment to be made.

Table 4.1

(a) Factor group analysis for [Al(OH₂)₆]Cl₃

D ⁶ 3d	Alg	A2g	Eg	A _{lu}	A _{2u}	Eu	
Trans.	l	2	3	2	2	4	
Rotatory	1	l	2			ł	AlO ₆ Octahedron
Internal	. 2	2	4	3	3	6	
ρ _w	l	l	2	l	l	2	Modes due
ρ _r	l	l	2	l	1	2	water molecules
ρ _t	l	l	2	l	l	2	
δ	l	l	2	l	1	2	
ν	2	2	4	2	2	4	
Total	10	11	21	11	12	23	
Activity	x^2+y^2 z^2		x ² -y ² xy, xz		Z	x,y	
			y zu				

Trans = optic branch translatory modes, acoustic modes have been subtracted; Rotatory = optic branch rotatory modes; Internal = modes due to Al-O band stretching and deformations = sum of a. ρ_w , ρ_r , ρ_t numbers of wag, rock and twisting modes of coordinated water; δ = bending modes of coordinated water; ν = stretching modes of coordinated water. Table 4.1

(ь)

Correlation scheme for AlO_6

Oh	Site, $S_6 \xrightarrow{x^2}$	Crystal, D ⁶ 3d
ν ₁ (A _{1g})	Ag	$A_{1g} + A_{2g}$
ν ₂ (E _g)	Eg	2Eg
ν ₅ (T _{2g})	$A_g + E_g$	$A_{1g} + A_{2g} + 2E_{g}$
ν ₃ (T _{1u})	A _u + E _u	$A_{1u} + A_{2u} + 2E_u$
ν ₄ (Τ _{1u})	$A_u + E_u$	$A_{1u} + A_{2u} + 2E_{u}$
ν ₆ (T _{2u})	$A_u + E_u$	$A_{1u} + A_{2u} + 2E_{u}$

e ^{III} Cl ₅ (OH ₂)] 600 Fe ^{III} Cl ₅ (OH ₂)] 540 (430) Mn ^{II} Cl ₄ (OH ₂) ₂] 570 (430) Ni ^{II} Cl ₄ (OH ₂) ₂] 621	р _r 460 455 (350) 471	v(M-OH, 390 320 (310) 295 (282) 353	290 290 342	Reference Adams and Lock (1971) Shankel and Bates (1976)
$n^{IIIF_{4}}(OH_{2})_{2}$] 730 [°] (525)	665 (470)	370 (367)		Bukovec and Kaucic (1977)

 $^{\rm a}$ Authors preferred not to distinguish between $\rho_{\rm W}$ and $\rho_{\rm r}.$ Deuteriated data is shown in parentheses.

.

Table 4.3

(a) I.r. reflectance data - T.O. frequencies/cm⁻¹ for single
 crystal AlCl₃.6H₂O and AlCl₃.6O₂O (in parentheses) at 295 K.



(ь)

Mull spectrum of $AlCl_{3.6H_2O}$ at liquid nitrogen temperature

m = medium; sh = shoulder; s = strong; w = weak

^a Shape of the reflectance band and Kramers-Kronig analyses are inconsistent; this may indicate the presence of an extra band <u>218</u> in protiate, mull spectrum shows an additional peak in this region.

Table 4.4

(a) Single crystal Raman data cm^{-1} and intensities (arbitrary units) for AlCl₃.6H₂O, using 514.5 nm radiation at 115 K.

```
Region of table (a) A_{lg} modes recorded at slit width 1.5 cm<sup>-1</sup>
E_g modes recorded at 2.4 cm<sup>-1</sup>
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Region of table (b) A_{lg} modes recorded at slit width 3.3 cm⁻¹ E_{σ} modes recorded at 4.7 cm⁻¹

(b) Single crystal Raman data cm⁻¹ and intensities (arbitrary units) for AlCl₃.60₂0, using 514.5 nm radiation at 115 K.

Region of table (a) All modes recorded at slit width 1 cm⁻¹ Region of table (b) All modes recorded at slit width 2.85 cm⁻¹

 $v_{\rm R}$ = Rotatory modes of [Al(OH₂)₆]³⁺

 v_{π} = Translatory modes

units) for single crystal $AlCl_3$. $6H_2O$.

cm ⁻¹	Symmetry species	y(zz)x	y(xy)x	y(xz)x	y(zy)x			
71	Eg		20	40	15	Ì]
78	Alg	15				5	v _R	
110	Eg		15	22	10]		
128	Eg		74	100	35			
138	Eg		37	50	20	ł	ν _T	
150	Eg		18	30	14			
183	Alg	100	8	10	13	J		
295	Alg	42				}.	ν ₅	
310	Eg		50	80	33	J		
432	Eg		5	14	5		ν2	
524	Alg	5				•	ν1	
534	Eg		5	8	3			
566	Eg		10	10	5			
584	Alg	10						
610	Eg		8	30	7	ļ	H ₂ O	
622	Eg		6	35	8		librations	
701	Alg	15						
800	A _{lg} +E _g	30		5	10			
825	Eg		15	12	12	J)
1094	Alg	15					overtone	
1645	Eg+Alg	3	8	10	6	ר	δ(ОН)	
3045	Eg		13	80	30			
3053	Alg	45				ł	ν ₁ (H ₂ O)	2(6)
3076	Eg		18	11		J		
3162	A _{lg}	3					ν ₃ (H ₂ O)	
							/	

cm ⁻¹	Symmetry species	y(zz)x	y(xy)x	y(xz)x	y(zy)x	
71	Eg		7 0	25	25	
78	A _{lg}	20				
109	Eg			12	13	
128	Eg		80	48	50	
139	Eg			30	30	(a)
149	Eg		15	15	14	
180	Alg	90				
284	A _{1g}	30	,			
291	Eg		20	30	25	J
418	A _{1g} +E _g	10	15	10	8)
443	Eg		10	10	8	
497	A lg	10				
504	A _{lg} +E _g	15	7	6	4	(b)
593	A _{lg}	8				
617	Eg		15	8	5	
650	Alg	12				
820	Eg		5	6	5	Į
1458	Eg					
2272	Eg		60	60	60	
2309	A _{lg}	85				
2320	Eg		28	25	25	> (a)
2416	A _{lg}	18				
3086	A _{1g} +E _g	12	10	10	10	
						ノ

Table 4.5	Comparison	of modes of vibrati	ion of $[M(OH_2)_6]^{n+}$
	Al(OH ₂) ₆ 3+ (a)	Ni(OH ₂)6 ²⁺ (b)	Mg(OH ₂) ₆ 2+ (c)
v1	524	382	363
ν2	432	301	310
ν ₃	570 or 653	333, 381	421
Vų	316, 327	209, 207	200-215 (4 bands)
ν ₅	295, 310	209, 191	268-285 (5 bands)
ν ₆	205, 224, 250	142, 146	

(a) This work.

(b) Jäger and Schaack (1973).

(c) Hillaire <u>et al</u> (B) (1971).

FIG. 4.1











 $v(X-\bar{Y})$







FIG. 4.3





Figures 4.5-4.6

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AlCl₃.6H₂O

Figure 4.5 A_{2u} 295 K

Figure 4.6 E_u 295 K







FIG. 4.8



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Chapter Five

Far-i.r. Spectra of Mercuric Chloride

and Mercuric Bromide

Both mercuric chloride and bromide have been extensively studied using Raman (reference list 1) and i.r. spectroscopy (reference list 2).

The majority of the data obtained has been confined to the positions of the stretching modes allowed in D_{oh} molecules, these are: v_1 , Σ_g^+ , $v(Hg-X)_{sym}$; and v_3 , Σ_u^+ , $v(Hg-X)_{asym}$, and these have been assigned beyond doubt for gaseous, molten, and dissolved samples, mainly on the basis of the Raman polarisation property of v_1 ; v_3 may be assigned by elimination or by using force constant relations.

Information on the position of v_2 (π_u , $\delta(HgX_2)$) was first obtained from the analysis of the fine structure of the electronic spectra of the vapours of the compounds; (Wehrli 1938, 1940) and Sponer and Teller (1941) calculated values of v_2 in the region of 70 cm⁻¹ for HgCl₂ and 41 cm⁻¹ for HgBr₂. These values are very low, and have subsequently been corrected after the observation of v_2 in far-i.r. gas phase spectra by Malt'sev <u>et al</u> (1971). Matrix-isolation studies by Loewenschuss, Ron and Schepp (1969) support these values; they obtained values of v_2 of 107 cm⁻¹ for HgCl₂, and 73 cm⁻¹ for HgBr₂. These compare favourably with values of 100 cm⁻¹ for HgCl₂ and 68 cm⁻¹ for HgBr₂ obtained by Malt'sev et al. These values are taken as determined. Studies of the solids were, until fairly recently, fragmented and incomplete. Rao (1941) first reported low frequency Raman data on HgCl₂ observing bands at 73, 95, and 124 cm⁻¹. He concluded that the lowest band may have been the v_2 mode, the others lattice modes. The complete frequency range single crystal Raman spectrum of HgCl₂ was obtained by Brahms and Mathieu (1960), and a few, relatively minor, corrections were added by Poulet and Mathieu (1963). Both studies were conducted at ambient temperature. The frequency shifts on cooling to low temperatures may be inferred from data collected on a polycrystalline sample at 77[°]K by Decamps <u>et al</u> (1973). No single crystal Raman study of HgBr₂ has been published to date, however, Decamps <u>et al</u> (1973) list bands observed from a polycrystalline sample at 77[°]K.

I.r. information on both $HgCl_2$ and $HgBr_2$ is extremely fragmented; there are many reports in the literature of i.r. absorption experiments (reference list 2); of those which concern the solid state, few give data in the region below the stretching modes v_1 and v_3 , and none has involved the use of polarised radiation. Accordingly, no firm data is available on which to base a unique assignment of either $HgCl_2$ or $HgBr_2$ in the i.r. In addition, it is doubtful whether the spectra have been fully established in the past.

Experimental

Samples of commercial grade HgBr2 and HgCl2 were purified by two successive vacuum sublimations. Crystals were grown by vapour-phase deposition of the purified sublimates. A full description of the apparatus used is found in Chapter Two, section B. The tubes were evacuated to a pressure of 10^{-2} torr using a rotary vacuum pump, and were pulled through a thermal gradient at a rate of extrusion of ca. 1 cm per day. Peak temperatures were for HgCl₂ (130°C) and HgBr₂ (110°C). Each boule of crystalline sublimate was cut into sections and polished, to expose developed faces which showed indicatrix directions under a polarising microscope. Axes corresponding to indicatrix directions were identified using X-ray methods and labelled according to the standard axis set given in "International Tables for X-Ray Crystallography". Accordingly the axes chosen were :

> HgCl₂ $a_0 = 12.735 \text{ Å}$; $b_0 = 5.963 \text{ Å}$; $c_0 = 4.325 \text{ Å}$ HgBr₂ $a_0 = 4.624 \text{ Å}$; $b_0 = 6.798 \text{ Å}$; $c_0 = 12.445 \text{ Å}$

The sample of $HgCl_2$ used to collect data by i.r. reflectance measured 5(x) x 3(z) x 2(y) mm, and the sample of $HgBr_2$ used, also for reflectance, measured 15(z) x 6(x) x 3(y) mm. Axes are shown in parentheses.

The majority of the data collected was by using reflectance spectroscopy. This is because both compounds are highly absorbing in the far-i.r. and have measurable vapour pressures at room temperature. As the instrument used (FS720) is a single beam instrument, and therefore has to be evacuated to pressures of $v10^{-2}$ torr for collecting data, it was felt that the sufficiently thin slices of crystal necessary for transmission experiments would probably sublime under the influence of the vacuum at ambient temperatures. Some transmission experiments were conducted using the cleavage fragments of <u>ca</u>. 1.5 mm² exposing in both cases the (xz) face of the crystals. For HgCl₂ this face contains the directions which locate v_1 and v_3 , for HgBr₂ only one direction on this face contains v_1 and v_3 . Repeated attempts to obtain cleavage fragments containing the (yz) or (xy) faces failed due to the extreme softness of the material.

Samples for reflectance were mounted onto copper blocks using a quick-setting epoxy resin. It was found that if aluminium powder was incorporated into the resin the samples decomposed over a period of 4-5 h, and was therefore not used. Using a home-made liquid nitrogen cryostat temperatures of 115⁰K were obtained at the samples.

Several attempts were made to obtain single crystal Raman data on both compounds, using all 3 scattering geometries and an immersion cell. Neither compound showed any significant intensity changes with orientation. This is attributed to
the existence of micro-domains within the crystals, although this was not evident in the examination with a polarising microscope.

Theory

WycKoff (1964) has reported the X-ray structure determinations of both compounds, but he uses a non-standard nomenclature. When corrected to the standard setting given in "International X-Ray Tables" this gives:

> HgCl₂ symmetry Pnma \equiv D¹⁶_{2h} with z = 4 HgBr₂ symmetry Cmc2₁ \equiv C¹²_{2v} with z = 2

both compounds crystallise in the orthorhombic system.

Both compounds are composed of molecules stacked in planar sheets parallel to one crystallographic axis. The two Hg-X bands are not required to be either equal in length or colinear, however, the actual distortions are sufficiently small to allow $D_{\infty h}$ to form the basis of an understanding of the spectra.

The factor group analyses have been reported previously by Adams and Appleby (1977) (6/2230) and (7/079) for $HgCl_2$ and $HgBr_2$ respectively. $HgCl_2$ has all atoms on sites 4c and the molecular sheets are stacked parallel to the b axis. $HgBr_2$ has all atoms on sites 4a, molecular sheets are stacked parallel to the a axis. Factor group analyses are shown in Tables 5.1 and 5.2, and a correlation scheme for both molecules is shown in Table 5.3.

Results and discussion for HgCl₂

The f.g.a. in Table 5.1 shows that the vector of optically active modes allows for:

$$6A_{g} + 3B_{1g} + 6B_{2g} + 3B_{3g} + 5B_{1u} + 2B_{2u} + 5B_{3u}$$

g modes are Raman active, u modes are i.r. active

If it is assumed, for the purposes of accounting for the number of modes, that these may be decomposed into internal and external modes

$$N_{(internal)} = 3A_g + B_{1g} + 3B_{2g} + B_{3g} + 3B_{1u} + B_{2u} + 3B_{3u}$$

 $N_{\text{trans}} = 2A_{g} + B_{1g} + 2B_{2g} + B_{3g} + B_{1u} + B_{3u}$ $N_{\text{rotatory}} = A_{g} + B_{1g} + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$ "external" modes

It can be seen from the correlation scheme (Table 5.3) that ν_2 is active in each species, ν_3 and ν_1 are active only in A_g , B_{2g} , B_{1u} and B_{3u} .

If attention is confined to i.r. active modes, theory predicts that:

 $B_{1\rm u}$ will contain 3 internal modes ($\nu_1,\,\nu_2$ and $\nu_3)$ as well as 1 rotatory and 1 translatory mode.

 $B_{\mbox{2}\,\mbox{u}}$ will contain 1 internal mode (ν_2) and 1 rotatory only.

 B_{3u} will contain 3 internal modes (v_1 , v_2 and v_3), 1 translatory and 1 rotatory (as B_{1u}).

Results are shown in figures 5.1, 5.2, and 5.3, and data summarised in Table 5.4.

With the exception of the B_{3u} Davydov component of v_1 , which was only observed in reflectance at low temperature, all the predicted components of v_1 and v_3 are clearly observed at room temperature (region >200 cm⁻¹). The polarised behaviour of the weak v_3 modes was confirmed by transmission measurements through a thin cleavage fragment containing the (xz) face. All other modes showed total adsorption in the range studied. Incorporating this data with that of Brahms and Mathieu (1960), a full assignment of v_1 and v_3 modes is possible.

	Ag	B _{2g}	B _{lu}	B ₃ u	Average	Vapour	Δvcm ⁻¹
v1	310	316	312	330	317	360	-43
ν ₃	n.o.	375	379	372	375	413	-38

The frequencies obtained by Klemperer and Lindemann (1956) taken in the gas phase, are used as a standard to calculate the shift Δv , which is a measure of the effect of taking an isolated molecule and incorporating it into the crystal. The subscripts 2 and 3 of the data obtained by Brahms and Mathieu (1960) for their symmetry species are interchanged to conform with the standard setting which is used here. The forms of the Davydov components of v_1 are shown in figure 5.7(a).

The region below v_1 and v_3

This region presents a more difficult problem of assignment, as it contains translatory and rotatory modes in addition to components of v_2 . The only adequate far-i.r. data collected on solid HgCl₂ is that of Decamps and Hadni (1968). They reported a weak doublet at 32 and 39 cm^{-1} , followed by bands at 75.5 (sharp) and 97 (broad) cm⁻¹, in an unoriented study. Other reports by Mikawa et al (1966) and Adams and Appleby (1977) (6/2230) give various estimates of the band above 75.5 cm^{-1} which is confirmed in both cases. The reflectance data reported here shows that this region is a composite of five bands with T.O. frequencies of 94, 96, 108, 115 and 123 cm^{-1} . The modes reported by Decamps and Hadni at 32 and 39 cm⁻¹ were observed as weak features distorted by the neighbouring high intensity reflectance bands. In transmission measurements, these bands were clearly observed and their polarisation behaviour was seen to conform with that seen in the reflectance spectra. The modes above ca. 70 cm⁻¹ showed total absorption and no accurate estimate of their maxima could be taken.

The Raman data of Poulet and Mathieu (1963) in this region, show bands in a similar pattern to the i.r. spectra.

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If the i.r. data collected here is considered along with the Raman evidence an assignment can be attempted.

Theory predicts that the B_{2u} spectrum will contain only v_2 and a rotatory mode. T.O. frequencies were calculated at 94 and 115 cm⁻¹, although which is which cannot be ascertained.

Both B_{1u} and B_{3u} spectra are predicted to contain a v_2 component, one rotatory and one translatory mode each. At ambient temperatures the B_{1u} spectrum contained bands at 40, 74, and 108 cm⁻¹; however, on cooling to 115° K, the mode at 108 cm⁻¹ is seen to split into a doublet with T.O. frequencies of 113 and 127 cm⁻¹, thus providing one more than the theoretically allowed number. Two alcernatives can be forwarded to account for this behaviour.

i) The three B_{Iu} bands at 76, 113, and 127 cm⁻¹ at $115^{\circ}K$ are all fundamentals, this means that in the same region B_{3u} is accidentally short of one band. This forces the implication that the absorption at 32 and 40 cm⁻¹ are not fundamental modes of vibration.

ii) The band at 127 cm^{-1} at 115°K is due to two-phonon processes, all others are fundamental modes of vibration.

The Raman data of Poulet and Mathieu (1963) records bands at 16, 25 and 45 cm^{-1} as well as higher frequencies; 128.

it is unlikely that they are all due to two-phonon processes. Adams and Appleby (1977) (6/2230) have confirmed these low frequency features. Since B₂₁₁ contains no translatory mode, and no band is observed below 90 cm⁻¹, the bands at 32 and 40 cm⁻¹, in B_{1u} and B_{3u} respectively are taken as being of translatory origin. This fits well with Raman counterparts at 16 cm⁻¹ $(B_{3g} + B_{2g})$, 25 cm⁻¹ (A_g) and 45 cm⁻¹ (B_{2g}). There is no <u>a</u> priori evidence on which v_2 modes, and those of rotatory origin can be distinguished, if such a distinction is valid. Gans (1971) has discussed the displacements involved, as they are similar it is possible that these will couple strongly, however, this is not certain. The gas phase data of Malt'sev et al (1971) and the matrix studies of Loewenschuss et al (1969) place v_2 at <u>ca.</u> 100 cm⁻¹; therefore the modes at 120 (A_g), 126 (B_{1g}), 108 (B_{1u}) , 115 (B_{2u}) and 123 (B_{3u}) may be considered as having a major contribution from v_2 . Modes at 72 ($B_{1g} + B_{3g}$), 75 ($A_g + B_{3g}$) B_{3g}), 74 (B_{1u}), 94 (B_{2u}) and 96 (B_{3u}) can be assigned as being principally rotatory in type. This assignment for v_2 can only be confirmed by a full N.C.A. treatment of the lattice.

Results and discussion for HgBr

The F.G.A. in Table 5.2 shows that the vector of optically active modes allows for:

$$5A_1 + 3A_2 + 2B_1 + 5B_2$$

all modes are Raman active and all but A2 are also i.r. active.

If it is assumed, for the purposes of accounting for the number of modes, that these may be decomposed into internal and external modes

 $N_{(internal)} = 3A_1 + A_2 + B_1 + 3B_2$ $N_{TRANS} = A_1 + A_2 + B_2$ $N_{ROTATORY} = A_1 + A_2 + B_1 + B_2$

It can be seen from the correlation scheme (table 5.3), that v_2 is active in each species, and that v_1 and v_3 are active only in A₁ and B₂.

If attention is confined to i.r. activity theory predicts that: A₁ will contain 3 internal modes (ν_1 , ν_2 and ν_3) as well as 1 rotatory and 1 translatory mode,

 B_1 will contain 1 internal mode (v_2) and 1 rotatory only. B_2 will contain 3 internal modes (v_1 , v_2 and v_3), 1 rotatory and 1 translatory.

Selection rules require that i.r. and Raman components are coincident. The v_3 components have been established to be in the region of <u>ca</u>. 250 cm⁻¹, and v_3 <u>ca</u>. 180 cm⁻¹. Since all lattice modes and all Davydov components of v_2 are in the range <80 cm⁻¹, it is suggestive of a much stronger intermolecular attraction than HgCl₂, and there may be no meaningful distinction between the modes labelled above.

Results are shown in figures 5.4, 5.5, 5.6 and data αre summarised in Table 5.5.

The Raman spectra obtained are of extreme simplicity, showing only 2 major features, one intense band is located at 187 cm⁻¹ which is v_1 , (v(Hg-Br)_{svm}) and another intense band at 57 cm⁻¹; Adams and Appleby (1977) (7/079) have observed some weak features at 15 and 18 cm⁻¹, and some less well-defined scatter at ca. 40 cm⁻¹. Decamps et al (1973) have shown that the 57 cm⁻¹ band splits into two components at low temperature 58 and 59 cm^{-1} , also they reported observing the 18 cm^{-1} band. No single crystal Raman data is available, and this study was unable to obtain any significant intensity changes with orient-As the factor group is non-centrosymmetric the Raman ation. spectra may show L.O. components (see Chapter Two, Section B) in addition to the T.O. modes predicted by F.G.A. Such features may be identifiable by the coincidence with L.O. mode frequencies obtained from the Kramers-Kronig analysis of the reflectance data.

Decamps and Hadni (1968) obtained some results for the far-i.r. of solid HgBr₂ using unpolarised transmission measurements. They observed v_3 as a single band centred at 250 cm⁻¹, with a very weak feature assigned to v_1 at 185 cm⁻¹. A mull spectrum reported by Nyguist and Kagel (1971) did not show the feature at 185 cm⁻¹, however Décamps <u>et al</u> (1973) did observe this

feature at low temperature, as well as the resolution of v_3 into a doublet at 230 and 248 cm⁻¹.

In the reflectance results reported here, v_1 was not seen in either A_1 or B_2 spectra even at 115 K. It was observed in the A_1 spectrum in transmission measurements through a cleavage fragment containing the (xz) face at 187 cm⁻¹, which is coincident with the Raman feature of the material.

Analysis shows that the v(Hg-Br) mode which is prominent in i.r. mulls at 252 cm⁻¹ is the A₁ Davydov component of v_3 . The much weaker B₂ component is centred at 220 cm⁻¹. The average of these two values, 236 cm⁻¹, may be compared to the value obtained by Klemperer and Lindemann (1956) from the vapour which is 293 cm⁻¹. The static field shift Δv is -57 cm⁻¹ in this case. Similarly Δv for v_1 can be estimated at -38 cm⁻¹, as the gas phase value is 225 cm⁻¹. These shifts are comparable to those calculated for HgCl₂. The forms of the v_1 Davydov components are shown in figure 5.7(b).

The region below v_1 and v_3

Decamps and Hadni (1968) obtained values of 35, 53 and 71 (broad) cm^{-1} in a transmission study using unpolarised radiation. Decamps <u>et al</u> (1973) resolved these features at low temperature and obtained values of 32, 55, 65, 86 and 113 cm^{-1} , unfortunately no intensities are given.

Theory predicts that the B1 spectrum will be a simple one, containing only a Davydov component of v_2 and a rotatory mode. At both ambient and low temperature two intense - almost coincident reflectance maxima were observed. This appeared to be a doublet with T.O. frequencies of 33 and ca. 50 cm⁻¹. Transmission spectra obtained with the (xz) face cleavage fragment, showed only a very intense absorption from ca. 15-90 $\rm cm^{-1}$. This could be imagined to be resolved into two components, which is consistent with reflectance results. The exact nature of this reflectance spectrum is still not absolutely clear, Kramers-Kronig analyses could not separate the reflectance maxima to give two T.O. frequencies. Simple harmonic oscillator analyses were unable to reproduce the spectrum adequately. It was deduced that two bands were present, and that these are the F.G.A. fundamentals.

Both A_1 and B_2 should exhibit three low frequency bands. Each contains a v_2 component, 1 rotatory and 1 translatory mode. The A_1 reflectance spectrum showed bands with T.O. frequencies of 30 and 70 cm⁻¹. Transmission measurements confirmed the weak band at 29 cm⁻¹, and revealed in addition another sharp band at 15 cm⁻¹, coincident with a weak Raman feature which is accordingly given A_1 symmetry.

The B₂ spectrum revealed bands at 42, 53 and 79 cm⁻¹, the feature at 42 cm⁻¹was only clearly seen at 115 K.

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Exactly the number of bands predicted by F.G.A. have been observed, apart from A_2 species. When superimposed they account for all of the observed features of the mull spectrum, although any attempt at a unique assignment is extremely tentative.

It remains to assign the Raman bands not found to be coincident with i.r. bands. The band at 18 cm⁻¹ is assigned to A_2 , which is unique to the Raman spectrum, and could be the required translatory mode. The weak scatter at <u>ca</u>. 40 cm⁻¹ is taken to be the counterpart of the B_2 band found in the i.r., although the breadth of this band may be taken to imply an L.O. component in addition. The Raman band at 57 cm⁻¹ is almost coincident with the B_2 *i.r.* band at 53 cm⁻¹. The resolution of this into components at low temperatures raises a problem which can only be resolved by a single crystal Raman spectrum of the compound. Three explanations are possible:

i) The new Raman band is an A_1 L.O. component, and as such it should be coincident with an L.O. determined from the A_1 reflectance spectrum analysis; it is not, and this theory is therefore rejected.

ii) It is one of the A_2 components yet to be identified; this is regarded as probable.

iii) It represents another genuine A_1 fundamental; if this is so the 15 cm⁻¹ band found in transmission must be rejected and treated as an artefact. In view of the difficulties in obtaining i.r. spectra at such low frequencies, it is desirable that the 15 cm⁻¹ be confirmed using a lamellar-grating instrument.

It is unlikely that v_2 will drop in frequency substantially from that calculated for it in a krypton matrix, i.e. 73 cm⁻¹ (Loewenschuss <u>et al</u> 1969) for the crystalline state. It is therefore probable that the bands at <u>ca</u>. 75 cm⁻¹ in the crystal receive a large contribution from v_2 , i.e. 76 (B₂), 70 (A₁) and 50 (B₁). This automatically describes the features at 53, 33 and 30 cm⁻¹and, in particular, the 57 cm⁻¹ Raman feature as principally rotatory in type. This accords well with the origin of the 57 cm⁻¹ feature in the π_g (Raman active) species of D_{ooh} , and would therefore be expected to show strong Raman activity.

The implication of this theory is that the coupling between v_2 and rotatory modes is relatively weak and allows a distinction to be made between them. Any assignment can only be confirmed by a full N.C.A. treatment of the lattice.

Table 5	Ĵ.	1
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Factor group analysis for HgCl₂.

D ₂ h	N _T a	т _А	T R	(x,y)	N int	Activity
Ag	6		2	1	3(v1,v2,v3)	x^2, y^2, z^2
^B lg	3		1	1	1(v ₂)	xy Raman
B ₂ g	6		2	l	3(v1,v2,v3)	xz
B _{3g}	3		1	1	1(v ₂)	yz
Au	3		l	l	1(v ₂)	
^B lu	6	l	1	1	3(v1,v2,v3)	z
B _{2u}	3	1	0	1	1(v ₂)	y { I.r.
B _{3u}	6	1	1	1	3(v1,v2,v3)	x

 $\frac{a}{T} = 1$ N_T = total number of modes in the unit cell. T_A = acoustic branch modes. T = optic branch translatory modes. R(x,y) = rotatory lattice modes. N_{int} = number of internal modes and descriptions (see Table 5.3).

Table	5	•	2
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Factor group analysis for HgBr₂.

12 C _{2v}	N _T a	т _А	Т	R(x,y)	N int	Activity
A ₁	6	l	l	l	3(v1,v2,v3)	$z x^2, y^2, z^2$
A ₂	3		1	l	l(ν ₂)	ху
Bı	3	l		·l	1(ν ₂)	x zx
B ₂	6	l	1	1	3(v ₁ ,v ₂ ,v ₃)	y yz

 $\frac{a}{T}$ N_T = total number of modes in unit cell.

 T_A = acoustic branch modes.

T = optic branch translatory modes.

R(x,y) = rotatory lattice modes.

N = number of internal modes and descriptions
(see Table 5.3).

Table 5.3

Correlation schemes for HgCl2 and HgBr2.



Approximate geometry, neither molecule has strict $\mathtt{D}_{\mathbf{w}h}$ symmetry in the solid state. ر م

 $\stackrel{\rm D}{=}$ All g modes are Raman active, $B_{\rm nu}$ modes are i.r. active.

^C All modes are Raman active, only A₂ modes are not i.r. active.

Table 5.4 Transverse and longitudinal optic mode frequencies/cm⁻¹ for HgCl₂, derived from Kramers-Kronig analyses of i.r. reflectance spectra.

^B 1u ^(z) 295 K		115	К	Assignment—
T.O.	L.O.	Т.О.	L.0.	
∿39 <u>b</u>	<u>∿</u> 44	39	44	ν _T
74	83	76	85	v_2 , $\delta(HgCl_2)$; or v_R
108 <u>d</u>	133 <u>d</u>	113 <u>d</u>	137 <u>d</u>	v_{R} or v_{2}
310 <u>f</u>	316	310	316	v_1 , $v(Hg-Cl)_{sym}$
379	388	384	392	ν ₃ , ν(Hg-Cl) _{asym}
B _{2u} (y)	ĸ	115	ĸ	
T.O.	L.O.	T.O.	L.O.	
94	∿107 <u>-</u>	96	∿112 ^C	ν2, δ(HgCl ₂); or ν _R
115	132	120	134	v_{R} or v_{2}
в _{зи} (х) 295 К		115	к	
Τ.Ο.	L.O.	Т.О.	L.O.	
30 4	35	32	37	ν _T
96	112	99	116	v_2 , $\delta(HgCl_2)$; or v_2
123	130	127	136	v_{R} or v_{2}
n.o. <u>f</u>	n.o.	330	334	ν ₁ , ν(Hg-Cl) _{sym}
372	386	380	390	v_3 , $v(Hg-Cl)_{asym}$

 $\frac{a}{2}$ At 32 cm⁻¹ in single crystal transmission at 295°K.

 $\frac{b}{1}$ At 40 cm⁻¹ in single crystal transmission at 295°K, only clearly seen in reflectance at 115°K.

<u><u><u></u>C</u> Estimated visually.</u>

 $\frac{d}{d}$ Values obtained treating band as due to one fundamental only (see text) with a two-phonon mode at 127 cm⁻¹ at 115[°]K (figure 5.1). $\frac{e}{d} v_{T}$ = translatory mode, v_{R} = rotatory mode.

 $\frac{f}{2}$ Seen at 330 (B_{3u}) and 312 (B_{1u}) in single crystal transmission at 295^oK.

Table 5.5 Transverse and longitudinal optic mode frequencies/cm⁻¹ for HgBr₂, derived from Kramers-Kronig analyses of i.r. reflectance spectra.

A ₁ (z) 295 K ^d		к <u>d</u>	115 1	K	Assignment ^e	
Г	2.0.	L.O.	т.о.	L.O.	· · · · · · · · · · · · · · · · · · ·	
	15 a	-	-	-		
	30 <u>b</u>	33 ^C	31	33 ^C		
	70	100	73	104		
2	252	258	253	260	ν ₃ , ν(Hg-Br) asym	
$B_1(x)$	295	r	115 1	ĸ		
7	23.) [.0.	L.O.	T.O.	L.O.		
	33	93	35	96	ν _R or ν ₂ δ(HgBr ₂)	
م	-50	-	∿50	-	$v_2 \text{ or } v_R$	
в д (у))	V	י שונ			
ſ	295	к L.O.	T.O.	L.O.		
r	1.0. ·	n o.	42	44 <u>C</u>		
	53	70 <mark>-</mark>	53	70 ^{-C}		
	76	92	79	96		
2	220	-	222	234 <u>-</u>	ν ₃ , ν(Hg-Br) asym	

<u>a</u> Found in single crystal transmission only.

 $\frac{b}{29}$ cm⁻¹ in single crystal transmission.

<u><u><u></u></u> Estimated visually.</u>

 $\frac{d}{d}$ Additional feature found at 187 cm⁻¹ in single crystal transmission. $\frac{e}{d} v_{T} = translatory mode, v_{R} = rotatory mode.$









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FIG. 5.8a



FIG. 5.8b

Raman spectrum of $HgBr_2$ (Adams and Appleby 1977).











HgBr₂ Transmission



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List 1 (Raman Data)

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Chapter Six

Far-i.r. Spectra of Three Complex Halides

CsMgCl₃, CsMnBr₃, CsMnI₃

Introduction

A large number of double salts of the type AMX₃, where X = chloride or bromide; A = an alkalia metal (commonly Cs) and B = a divalent metal atom, adopt the CsNiCl₃ structure. This was determined by Tischchenko (1955), and is best described as a trigonal distortion of the perovskite structure adopted by many of the formally analogous complex fluorides - which has been extensively reviewed by Wells (1962). The octahedra share faces (as shown in figure 6.1). Crystals exhibit a good cleavage direction parallel to the c crystallographic axis.

There is to date little detailed spectroscopic data recorded on these compounds, which may be due to their hygroscopic nature. Single-crystal far-i.r. and Raman studies have been reported on some air-stable complex chlorides and bromides: CsNiCl₃ and CsCoCl₃ (Chadwick <u>et al</u> 1971); (CH₃)₄NMnCl₃ (Adams and Smardzewski 1971); and (CH₃)₄NNiBr₃ (Adams and Hall 1975). Although the last two crystals are not isomorphous with the first two, the geometries of the MX₃⁻ chains are very similar and have almost identical vibrational analyses. In all cases the assignments are unambiguous, frequency changes are due to the different masses of the atoms present. McPherson and Chang (1973) prepared and characterised a large number of chlorides, bromides and iodides of the type AMX₃. They found that in the vast majority of cases the CsNiCl₃ structure was adopted, except where for example M = Cu^{II}, the Jahn-Teller distortion is not compatible with Cu^{II} in perfectly octahedral sites. An i.r. mull comparison study of those compounds which had the CsNiCl₃ structure revealed that a change in cation had a relatively minor effect on the spectra; only the low frequency modes which principally involve cation translations showed significant changes. A change of halogen on the other hand, altered frequencies of all modes in the spectrum. A recent N.C.A. study of CsNiCl₃ by Adams, Christopher and Stevens (1977) has determined that the A_{2u} species modes are 98% pure modes involving only two atom types in each mode.

Theory

The structural determinations of $CsMgCl_3$ (Seifert and Ehrlich 1959), and $CsMnBr_3$ (Goodyear and Kennedy 1972) assign them to the hexagonal system with symmetry $P6_3/mmc \equiv D_{6h}^4$, which is the $CsNiCl_3$ structure. The structure of $CsMnI_3$ has not been determined to date, however, comparison with $CsNiCl_3$, $CsNiBr_3$ and $CsNiI_3$, which are isostructural, infers that it is isostructural with the bromide. The F.G.A. of $CsNiCl_3$ has been reported before (Adams and Smardzewski 1971) and is shown on Table 6.1.

Experimental

The crystals for this study were forwarded by Dr. G.L. Mcpherson of Tulane University, New Orleans. The crystals in all cases were
extremely water sensitive and readily decomposed into hydrated dihalides and alkali metal halides on contact with the atmosphere. The crystals were received sealed in quartz ampoules under dry nitrogen. It was decided to record i.r. spectra using reflectance techniques. This is because the compounds have been shown to be very strongly absorbing. Previous crystal studies : Chadwick <u>et al</u>; Adams and Smardzewski, and Adams and Hall; all resorted to reflectance techniques to obtain accurate absorption frequencies. Also the crystals may well have proved to be mechanically unstable in thin sections, due to their extreme hygroscopic nature.

Samples were prepared for both i.r. and Raman experiments in a dry box. The crystals used for Raman work were covered with a glass cap which was glued to the copper post (see Chapter Two section B). An atmosphere of dry nitrogen surrounded the samples at all times and crystals showed no signs of decomposition. Repeated attempts at single crystal Raman spectra were frustrated by an almost total lack of Raman scattered light, no useful data was collected. It has been noticed before in this laboratory that the presence of Mn^{II} in a compound often severely reduces the amount of Raman scattered light, the reason for which is not fully understood.

For the purposes of i.r. reflectance work, the samples were transferred from the dry box to the FS720 in sealed bottles.

The sample compartment and golay detector units of the 720 were encapsulated in polythene sheet; this formed a crude, but very effective, dry bag. The bottles were introduced into the bag via a small port which was immediately resealed. A large bowl of silica-gel dessicant was present in the bag at all times. The bag could be successively evacuated and flushed with dry nitrogen (passed over a drying column) by attaching a "T-junction", fitted with taps, into the vacuum line from the rotary pump to the sample compartment. One side of the "T-junction" was then connected to the vacuum line, the other to the nitrogen line; the outlet of the junction was connected to the sample compartment with pressure tubing. By opening the air bleed valve on the side of the sample compartment the atmosphere in the bag could be readily exchanged. After 30 minutes repeated evacuation and flushing, the bottles were opened, and the samples mounted into the holder with black insulation tape. The sample compartment was then immediately evacuated. The samples could be removed by filling the sample compartment with dry nitrogen via the "Tjunction" piece.

Attempts were made with all crystals to collect low temperature data. In all cases the interferrograms recorded were good, however, computed results showed signs of decomposition of the crystals. It can only be concluded that the most minute amounts of water present in the dynamic vacuum of the FS720

sample compartment, were sufficient to cause severe decomposition of the crystal surface used for gathering information. The problem is aggrevated at low temperatures by the fact that any water present will naturally condense onto the coolest part of the apparatus, i.e. the cooling block containing the crystal.

Results and Discussion

The vector of optically active modes allows for:

 $A_{1g} + E_{1g} + 3E_{2g} + 2A_{2u} + 3E_{1u}$

g modes are Raman active, u modes are i.r. active.

In all three cases $2A_{2u} + 3E_{1u}$ was found. The assignment follows unambiguously. A_{2u} contains one translatory mode, v_7 and one out of plane stretching mode, v_6 . E_{1u} contains one translatory mode v_{10} and two in-plane modes, v_8 and v_9 . The results for CsMgCl₃ and CsMnBr₃ are in good agreement with those obtained from i.r. mulls (Mcpherson and Chang 1973). The high frequency regions of all spectra are characterised by broad strong bands in transmission measurements. Adams and Hall (1975) and Chadwick <u>et al</u> (1971) had noticed that high frequency modes were sometimes significantly shifted in frequency from the estimates of transmission maxima to those obtained from Kramers-Kronig analyses; the latter were taken as the more accurate. It is believed that the values quoted here are the correct ones. Data **are** summarised in Table 6.2. The spectra for $CsMnI_3$ are identical in shape to those of the bromide, the frequencies are shifted to lower values, consistent with a change in atom mass. The symmetry of $CsMnI_3$ may reasonably be established as D_{6h}^4 with z = 2. The increase in respective frequencies for $CsMgCl_3$ over those of $CsNiCl_3$ is entirely consistent with the smaller mass of the Mg atom.

The E_{1u} modes seem more susceptible to a change in halogen than A_{2u} modes which is difficult to explain in the light of the N.C.A. treatment of CsNiCl₃ by Adams <u>et al</u> 1977. The A_{2u} modes are 98% pure modes involving 2 atom types only in each vibration; E_u modes are considerably mixed in character according to this scheme. It can only be assumed that some character involving halogen-halogen motions is significant in determining the frequency of E_{1u} modes. The alternative is that the N.C.A. treatment is in error.

The spectra of three chain structures have been established in the i.r. region. In order to obtain Raman results, a very sensitive system is required to overcome the very weak scattering of these materials.

I.r. active modes in some AMX $_3$ compounds.

Table 6.2

a Chadwick et al 1971.

D This work.

C Mcpherson and Chang 1973.

d Adams and Smardzewski 1971.

FIG. 6.1



Normal Modes of MX₃ Chain

CsNiCl₃ Structure























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Chapter Seven

Far-i.r. Spectra of Five Square-Planar

Complexes

AMX₄ A = κ^+ , $(NH_4)^+$ M = Pt, Pd X = Cl, Br

Introduction

There are many reports in the literature of spectroscopic studies on compounds of the type A_2MX_4 where : $A = K^{\dagger}$ or $(NH_4)^{\dagger}$; M = Pd^{II} or Pt^{II}; and X = Cl⁻ or Br⁻. A square planar (D_{4h}) ion such as $(PtCl_4)^{2^-}$ executes three i.r. active modes of vibration. They are : v_6 (E_u), v(Pt-Cl); v_7 (E_u), δ (Pt-Cl); ν_4 (A_{2U}), π (Pt-Cl), where δ and π represent deformations in and out of the plane respectively. In order to settle the order of the internal modes v_4 and v_7 , which are always close to each other, it is necessary to study single crystals in polarised i.r. radiation. This was done in the case of K₂PtCl₄ (Adams and Newton 1969) by single crystal transmission through a very thin slice of crystal. The order found was $\nu_7~({\rm E_u})$ > $\nu_4~({\rm A_{2u}}),$ in addition the three i.r. active lattice modes (see Table 7.1) were determined as $E_u > A_{2u} > E_u$. The exact value of v_4 was not determined because of what appeared to be a Fermi-resonance with a combination in the region ca. $170-200 \text{ cm}^{-1}$.

The analogous ammonium salts will be expected to exhibit modes due to ammonium rotation, however these are only active in the Raman effect (see Table 7.1). The intense colour and pleochroic nature of these crystals make Raman studies extremely difficult as the compounds tend to absorb the incident radiation very strongly and are easily decomposed with moderate irradiation. The lattice (translatory) modes of the ammonium salts are expected to occur at higher frequencies than the corresponding potassium salts, and might therefore be close in frequency to the v_4 and v_7 modes of the anion. A single-crystal Raman study of $(NH_4)_2PtCl_4$ and K_2PdCl_4 (Beattie and Gilson 1968) established an assignment for both.

The majority of data collected on these compounds is at room temperature on powder and solution samples. The results of Goggin and Mink (1974); Bosworth and Clark (1975); Hendra (1967); Hendra and Stratton (1969); Durig <u>et al</u> (1965); Fertel and Perry (1965); Poulet <u>et al</u> (1964); Sabatini <u>et al</u> (1964); Hiraishi and Shimanouchi (1966) and Perry <u>et al</u> (1967) have confirmed the assignments for the anions $(PtCl_4)^{2^-}$ and $(PdCl_4)^{2^-}$ unambiguously.

The first work on these compounds at temperatures below 100 K revealed additional bands on cooling (Adams and Berg 1976). These modes cannot be factor group fundamentals as these are all observed and accounted for at ambient temperature.

Experimental

Crystals of K_2PtCl_4 , K_2PdCl_4 , $(NH_4)_2PtCl_4$ and $(NH_4)_2PdCl_4$ were grown by slow evaporation of the respective aqueous solutions containing 10% HCl. Crystals of K_2PtBr_4 were grown in an analogous manner from a solution containing 10% HBr.

The crystals grew in the form of thick rods elongated along the c axis. Typical dimensions were $5 \times 3 \times 12 \text{ mm}^3$. The

largest face (e.g. 12 x 5 mm²) was used for reflectance measurements. The orientation of the crystals was established by examination with a polarising microscope. An indicatrix direction coincided with the longest side of the crystal in each case and this proved to indicate the c axis.

The lowest temperatures achieved for the single crystal studies was 145 K. The limit was imposed by the impossibility of enclosing the sample completely in a cold shield whilst allowing room for the incident and reflected beams. Mull spectra were obtained at temperatures down to 47.5 K (30 K for K_2PtBr_4).

Results and Discussion

The symmetry of K₂PtCl₄, K₂PdCl₄ and $(NH_4)_2$ PdCl₄ has been established as P4/mmm $\equiv D_{4h}^1$ with z = 1 (Dickenson 1922; Theilacker 1937; Bell <u>et al</u> 1966 and Mais <u>et al</u> 1972). In this structure the primitive unit cell is unimolecular, therefore the selection rules are those of the free ion.

 $(NH_4)_2PtCl_4$ is reasonably presumed to be isomorphous, this is supported by the similarity of the spectra. The studies of Kroening <u>et al</u> (1974) and Ito <u>et al</u> (1961) have established that K₂PtBr₄ is isomorphous also.

The assignment of $K_2PtCl_4 A_{2u}$ and E_u species confirm earlier results obtained with i.r. transmission (see Table 7.2).

The assignment of K₂PdCl₄ A_{2u} and E_u species (295 K) are in good agreement with those for K₂PtCl₄ when mass differences are considered. The order $v_7 > v_4$ is maintained, in addition the order of lattice modes $E_u > A_{2u} > E_u$ is seen to apply. Results are shown in figures 7.2 \rightarrow 7.5 and data are summarised in Table 7.2. The normal modes of the $(MX_4)^{2^-}$ ion are shown in Figure 7.1.

The i.r. spectrum of a chloroform solution of $(NBu_4^n)_2PtBr_4$ (Goggin and Mink 1974) showed a band at 105 cm⁻¹ with a shoulder at 112 cm⁻¹ in addition to v_6 at 227 cm⁻¹; almost the same frequencies were found for the solid. The assignment of v_4 at 105 cm⁻¹ and v_7 at 112 cm⁻¹ was made; only one lattice mode at 88 cm⁻¹ was found. The single crystal reflectance results for K_2PtBr_4 shown in Figures 7.6 \rightarrow 7.8 with data summarised in Table 7.3, show that v_4 and v_7 are almost coincident at 295 K (128 and 129 cm⁻¹ respectively). The two bands appeared as a single mode in mull spectra even at 30 K. The fact that this is a genuine result and not a failure to distinguish properly between orientations is shown by the good extinctions elsewhere in the spectra. The order of lattice modes is seen to obey that of K_2PtCl_4 and K_2PdCl_4 , i.e. $E_u > A_{2u} > E_u$. There must be considerable Fermi resonance between the E, lattice modes and v_7 , and the A_{211} lattice mode and v_4 , to have raised v_4 by 23 and v_7 by 14 cm⁻¹ above the values for the $(NBu_4^n)^+$ salt.

Mull spectra of the ammonium salts show a single band at ca. 120 cm⁻¹ readily attributable to one, or possibly more, translatory modes, a single v(M-C1) absorption ca. 320 cm⁻¹ and a very broad region of absorption in the intermediate range. The single crystal reflectance spectra for (NH4)2PdCl4 (Figures 7.11 and 7.12) show that there are two, almost coincident, lattice modes ($A_{2u} + E_u$) at \sim 123 cm⁻¹; a similar result is seen for (NH4)2PtCl4 (Figure 7.9 and 7.10) with bands at 116 cm⁻¹. Data are summarised in Table 7.4. The A_{2u} spectrum of (NH₄)₂PdCl₄ (295 K) shows in addition a band at 194 cm^{-1} which is attributed to v_4 in an analogous manner to K_2PtCl_4 and K_2PdCl_4 . The E_n spectrum (295 K) shows four modes as predicted by theory, two of these are required to be lattice modes. Two modes occur close to each other in the 150-200 cm⁻¹ range, only one occurs in the range attributed to the lattice modes. Two alternative interpretations may be given:

- (i) the single E_u band at 122 cm⁻¹ in (NH₄)₂PdCl₄ represents two, degenerate, lattice modes
- (ii) the 163 cm⁻¹ band may be attributed to the other predicted translatory mode.

This explanation is favoured here for the following reasons.

It is the simplest explanation of the data. In contrast, if the 122 $\rm cm^{-1}$ band is taken to represent two E_u modes it is

necessary to find an explanation for the additional band in the middle region, which can be ignored as the inability to distinguish between orientations as shown by the good extinctions elsewhere and it does not correspond to any A_{2u} mode. This view conflicts with the assignment of Adams and Berg (1976), based upon single crystal transmission spectra, in which the 122 cm⁻¹ band appeared to split into a doublet at low temperature; this is now regarded as an artefact in view of the difficulty of obtaining transmission measurements with highly absorbing materials such as these. Moreover, it is difficult to envisage the 163 cm⁻¹ band as due to interference from the substrate.

There is evidence from independent sources that translatory modes in ammonium salts are rather higher than in the corresponding potassium salts, as is expected from the relative masses. Thus in $(NH_4)_2SO_4$ and $(NH_4)_2BeF_4$ (Carter 1976, Popkov <u>et al</u> 1975) ammonium translational modes have been assigned in the 145-220 cm⁻¹ region. The associated rotational modes are much higher (\sim 350 cm⁻¹) and are not i.r. active in these compounds.

The assignment of E_u (translatory) at 122 cm⁻¹ and 163 cm⁻¹, a splitting of 41 cm⁻¹ (in (NH₄)₂PdCl₄), is to be compared with the splitting of 27 cm⁻¹ for the analogous modes in K₂PdCl₄. It is now clear that the breadth of the

central feature of the ammonium salts in mull spectra is due to the close proximity of three modes, possibly a reflectance component is included in the transmission envelope. There is also possibly some broadening due to hydrogen bonding with the Cl atoms of the anion.

The E_u spectrum of $(NH_4)_2PtCl_4$ shows a similar feature, however the shoulder at $\label{eq:however} consistent at <math>\label{eq:however} constant of the state of the expected of the exp$

Low temperature features

Adams and Berg (1976) reported that mulls of K_2PtCl_4 , K_2PdCl_4 , $(NH_4)_2PtCl_4$ and $(NH_4)_2PdCl_4$ develop new i.r. absorption features upon cooling. These modes can be immediately dismissed as due to ammonium rotational modes (even though theory forbids their i.r. activity) because the features are present in the potassium salts in which no cation rotatory modes are allowed.

The fact that these modes are genuine was proven by repeated data collection at a range of temperatures on different samples of the compounds. The results for K_2PdCl_4 (mull) are shown in Figure 7.13.

The low temperature reflectance spectra of K_2PdCl_4 clearly show new features at 145 K in both A_{2u} and E_u species; these correspond fairly well with those reported by Adams and Berg. The new strong features in the mull spectrum in the 250-320 cm⁻¹ range appear to have E_u symmetry. Mulls of K_2PtCl_4 whilst showing some new absorption at low temperature in this range never developed the structure or intensity shown in K_2PdCl_4 spectra. The reflectance spectra confirm this: there is a clear change of shape of the reflectance curve in the 200-300 cm⁻¹ region but no structure develops. This change in shape appears to affect the Kramers-Kronig analysis making the v(Pt-Cl) mode (E_u) appear abnormally weak in the ϵ ' and ϵ " functions, although it is strong in the reflectance curve.

Both $(NH_4)_2PdCl_4$ and $(NH_4)_2PtCl_4$ develop new features in their respective reflectance spectra at low temperatures, which are in close agreement with those reported by Adams and Berg.

(NH4) ₂ PdCl ₄	(NH4)	2PtCl ₄
(1)	(2)	(1)	(2)
312	-	305	304 (E _u)
308	309 (E _u)	284	282 (A _{2u})
298	295 (A _{2u} +E _u)		

(1) denotes the results of Adams and Berg (1976).(2) denotes this work.

It is obvious that an explanation to these phenomena needs to be given. The effect is strongest for the $(PdCl_4)^{2^-}$ anion, $(PtCl_4)^{2^-}$ shows a pronounced structure only in the ammonium salt; in contrast $(PtBr_4)^{2^-}$ shows no additional structure of any description either in mulls at low temperature or in reflectance spectra at low temperature.

The possibility that these modes are due to two-phonon processes cannot be ruled out, although it is unlikely since the modes are seen to gain intensity on cooling, this is the reverse of that expected. In both K_2PtCl_4 and K_2PdCl_4 no zone centre overtones are allowed since u x u = g x g = g but the following combinations can, in principle, result in i.r. activity, i.e. yield A_{2u} or E_u in the direct product:

 $\begin{array}{l} A_{2u} : A_{1g} \times A_{2u} ; A_{2g} \times A_{1u} ; B_{1g} \times B_{2u} ; B_{2g} \times B_{1u} \\ \\ E_{u} : E_{g} \times A_{1u}, A_{2u}, B_{1u} \text{ or } B_{2u} ; E_{u} \times A_{1g}, A_{2g}, B_{1g} \text{ or } B_{2g} \\ \\ \\ E_{g} \times E_{u} \text{ does not contain } A_{2u} \text{ and is therefore rejected.} \end{array}$

Inserting known frequencies, the following are the only combinations for K_2PtCl_4 and K_2PdCl_4 capable of giving frequencies in the 250-330 cm⁻¹ region:

The T (B_{2_u}) mode is inactive and is estimated at 100 cm⁻¹ for K₂PtCl₄ and 110 cm⁻¹ for K₂PdCl₄ and hence is unlikely to generate appreciable i.r. activity in combination with a Raman-activ; mode. R (A_{2g}) is also inactive and is estimated at 80 cm⁻¹ for K₂PtCl₄ and 71 cm⁻¹ for K₂PdCl₄. This leaves only two reasonable combinations, v₂ (B_{1g}) with the two E_u lattice modes; these are insufficient to account for either the number of or the correct frequency range for the new low temperature features of K₂PdCl₄. For the ammonium salts similar arguments apply. Identical combinations are feasible, in addition the combination of v₄ (A_{2u}) + R (E_g) (rotational mode for (MCl₄)^{2⁻}) yields a reasonable figure. The inactive T (B_{2u}) was estimated at 118 cm⁻¹ for (NH₄)₂PtCl₄ and 128 cm⁻¹ for $(NH_4)_2PdCl_4$. Rotational modes of ammonium must be considered also, a value of 250 cm⁻¹ was taken as an estimate. Although for the case of ammonium several modes could be inferred to have some activity none of them occurred in the correct frequency range. These results are taken as evidence to reject the theory that the features are not due to two-phonon processes.

The above argument implies that the new features cannot be adequately accounted for on the basis of the parent D_{4h}^{1} structure. The possibility of a phase transition must be considered. If the principle that new structures adopted will have the symmetry of a sub-group of D_{4h} is followed some new structures can be postulated. In addition it is necessary to consider structures in which:

(i) anions are rotated about the z, x or x' axes $(45^{\circ} \text{ to x and y axes})$

(ii) cations and anions are shifted relative to each other
(iii) the anions have a permanent distortion in the form
of one of the out-of-plane modes. Square planar
geometry for Pd^{II} and Pt^{II} is the norm but structures
such as cis[PtCl₂(PMe₃)₂] which has a tetrahedrally
distorted square planar structure are possible
(Messmer et al 1967).

Phase transitions are to be expected in ammonium salts by comparison with the behaviour of the ammonium halides (except the fluorides) which show complicated structural It must be considered that at low temperatures a behaviour. periodic hydrogen bonded array is formed. Such possibilities for the K₂PtCl₄ structure were considered by Adams and Berg, they concluded that for a unimolecular unit cell there were only two possibilities: D_4^1 and D_{2d}^1 . It is desirable that a consistent explanation for all the data is found, so that the new features in K2PdCl4 may be explained on the same basis of those of the ammonium salts. Adams and Berg reported that the D_{2d}^1 structure could be adopted by these structures for both a hydrogen bonded array and a $B_{l_{\mathrm{U}}}$ distortion of the square planar anion. This represents a very good explanation of the data and explains the trend that the intensity of the new features follows the order

 $(NH_4)_2$ PdCl₄ > K₂PdCl₄ > (NH₄)₂PtCl₄ > K₂PtCl₄

If the resistance of Pd^{II} to out of plane deformation is intermediate between that of Ni^{II} and Pt^{II}, any deformations would be reinforced by the hydrogen bonded array (where present.) Correlation from D_{4h} to D_{2d} shows that few Raman active modes can gain i.r. activity, too few to account for the number of new modes. For the ammonium salts where cation rotatory modes can gain activity it is doubtful if these occur in the correct frequency range.



The modes could only be explained on the basis of two-phonon modes in the D_{2d} structure. Adams and Berg tabulated various possibilities for the correct frequency range.

An X-ray study of the K₂PtCl₄ structure at various low temperatures in this laboratory (Appleby 1977) and a neutron diffraction study by Berg (1977) have revealed no evidence whatsoever for a phase change. It must be assumed that this hypothesis, although attractive, is in error. Although Adams and Berg are inclined to the view that this is the only feasible explanation of the data it must now be rejected. Another possible explanation is that the new features are derived from critical points in the Brillouin zone. Although i.r. photons have wavevector k $^{\circ}_{\nu}$ O they can interact with lattice phonons from throughout the zone in second order processes providing that

This can be achieved by the creation and annihilation of pairs of phonons with equal and opposite (but non-zero) wavevectors from critical points throughout the zone. The first Brillouin zone for K_2PtCl_4 is shown in Figure 7.14. This zone for a simple tetragonal Bravais cell contains many critical points; these are, with their respective point group symbols:

	Г	Λ	Δ	Σ	М	Х
	D4h	C _{4v}	c_{2v}	C _{2v}	C _{2v}	$c_{2_{\mathbf{v}}}$
(zoi	ne centre)		(y)	(y')	(y')	(y)

Y	R,U,W	A,V
C _s	Cs	C _s
(xy)	(zy)	(zy)

Iqbal <u>et al</u> (1972) have established a method of analysis to determine the origin of modes which are not factor group

fundamentals in the single crystal Raman spectrum of KNCS. The accuracy of this method has not yet been established. In outline the method entails the selection of external modes for the suitability of combination with an internal mode. Correlations are performed from the factor group of the structure to the point groups of the critical points of the zone. The representation of acoustic, translatory and rotatory modes are then obtained from the factor group analysis of the parent structure by correlation. The species of the point group which contain a contribution to the internal mode in this revised factor group analysis scheme are then selected as candidates for combination modes. I.r. activity is predicted on the basis of direct products between the species of the point group of the critical points (denoted G_k) which have a contribution to the internal If any of these products is one of the i.r. active mode. species of G_k the species is a candidate for a combination mode, for example:

The critical point Λ (C_{4v}) in K₂PtCl₄

Correlation from $D_{4h} \rightarrow C_{4v}$ gives

 $A_1 = A_{1g} + A_{2u}$; $A_2 = A_{2g} + A_{1u}$; $B_1 = B_{1g} + B_{2u}$ $B_2 = B_{2g} + B_{1u}$; $E = E_g + E_u$

In $C_{4v} A_1$ (z) and E (x,y) are the i.r. active species. From the F.G.A. scheme of the parent structure (see Table 7.1):

	т _А	T .	R .	v i	
Al	1	1	0	2	$(A_{1g} + A_{2u})$
A ₂	0	0	1	0	$(A_{2g} + A_{1u})$
B ₁	0	1	0	1	$(B_{1g} + B_{2u})$
B ₂	0	0	0	2	$(B_{2g} + B_{1u})$
E	1	2	1	2	(E _g + E _u)

 A_2 has no contribution to an internal mode and is therefore rejected. Direct products which yield A_1 from the remaining species are:

 $A_1 \times A_1 = A_1$; $B_1 \times B_1 = A_1$; $B_2 \times B_2 = A_1$; $E \times E = A_1$

In each case the representation of T_A , T, R is read for the second component of the direct product, i.e.

	т _А	Т	R
Al	l	1	0
Bl	0	l	0
B ₂	0	0	0
Е	1	2	1

The possibilities of combination with an internal mode are then acoustic and translatory components of A_1 ; a translatory component of B_1 ; an acoustic, two translatory components and **cae** rotatory component of E.

A similar calculation will yield possibilities for combinations via the E i.r. active species of $C_{4_{\rm V}}$.

It is obvious that if this calculation is performed for each critical point of the zone a very large number of possibilities emerge. The decision of the origin of each combination feature must be open to debate.

Although this theory cannot be rejected, much more work on these crystals is required before a definitive assignment can be made.

Some possibilities have been forwarded as to the origin of these new features on cooling, none of which yields an entirely satisfactory answer. In the absence of further experimental evidence there is no alternative but to admit that the origin of these modes is unknown.

Conclusion

The frequencies derived from the reflectance data reported here are preferred to those of mull spectra reported previously (Adams and Berg 1976). This is because it is felt that a reflectance component may distort the strongest bands. The data obtained for K_2PtCl_4 by single crystal transmission is open to suspicion because of the complications of Fermi resonance in the middle region of the A_{2u} spectrum. Both the lattice mode values and the ν (M-Cl) values obtained from the reflectance analysis are in very close agreement with values quoted for mull spectra.

There is a drop in v(Pt-C1) in passing from K_2PtC1_4 to the ammonium salt, and a considerable increase in v_4 $(+ 40 \text{ cm}^{-1})$ and v_7 $(+ 19 \text{ cm}^{-1})$, due to the hydrogen bonding in the ammonium salt, see Table 7.5. This is entirely expected since the Pt-Cl bond will be weakened but deformations of the Pt-Cl bond will become more difficult. Similar results are shown for the palladites. Simultaneously the ν_4 (A_{2u}), π (Pt-Cl) and ν_7 (E_u), δ (Pt-Cl) modes move closer together because these motions are both damped by hydrogen bonding. The effect of decreasing the temperature at the sample is to raise all the internal mode frequencies. The greatest shifts are seen in the ammonium salts (as expected) and is attributed to the increased strength of the hydrogen bonding. Similarly the lattice modes show a larger increase in frequency with decreasing temperature in the ammonium salts than in the potassium salts. The relative intensities of the lattice modes in all five complexes shows the same order and this supports the assignment of the lattice modes in the ammonium salts.

Factor Group Analysis for $A_2 MX_4$.



Internal modes of A (where applicable) have been omitted. T_A = acoustic branch modes ; T = optic branch translatory modes ; R^- = optic branch rotatory anion modes ; R^+ = optic branch rotatory cation modes ((NH₄)⁺ only) ; N₁ = internal modes of (MX₄)^{2⁻}.

- <u>Table 7.2</u> I.r. wavenumbers (cm^{-1}) for single crystal K_2MCl_4 obtained from Kramers-Kronig analyses of spectra.
- K₂PtCl₄

	293	5 K	145	K	а	
	т.о.	L.O.	Τ.Ο.	L.0.	Τ.Ο.	
A _{2u}	98	110	100	112	98	Lattice mode
	160	196	165	201	م170	ν ₄
Eu	86	96	88	100	87	Lattice mode
	113	126	114	128	112	Lattice mode
	185	204	186	208	194	ν7
	325	338	326	341	323	ν ₆

K_PdCl

L	т	295	к	145	К	
		Τ.Ο.	L.O.	Τ.Ο.	L.O.	
A _{2u}		106	120	110	122	Lattice mode
		162	200	162	200	v_4
				222 ^b	-	(see text)
				246 ^b	-	(see text)
Eu		92	100	94	105	Lattice mode
		114	134	118	137	Lattice mode
		178	196	184	196	ν ₇
		-	-	272 ^b	∿278	(see text)
		-	-	288 ^b	n300	(see text)
		334	350	338	358	v_6

^a Adams and Newton 1969 ; ^b New features seen at 145 K.

	295	К	145]	K	
	T.O.	L.O.	т.о.	L.O.	
A _{2u}	90	94	91	96	Lattice mode
	128	156	129	157	νų
Eu	75	96	78	97	Lattice mode
	102	109	106	113	Lattice mode
	129	145	133	142	ν ₇
	231	246	236	247	ν ₆

Table 7.3 I.r. wavenumbers (cm⁻¹) for single crystal K₂PtBr₄ obtained from Kramers-Kronig analyses of spectra.

Table 7.4I.r. wavenumbers (cm⁻¹) for single crystal(NH4)2MCl4 obtained from Kramers-Kronig
analyses of spectra.

(NH4)2PtCl4

	295	К	145	К	
	Τ.Ο.	L.O.	Т.О.	L.O.	
A ₂ u	116	123	118	125	Lattice mode
	200 ^a	270	207	250	v_4
	-	-	282	-	(See text)
^E u	116	133	124	133	Lattice mode
	sh	-	178	-	Lattice mode
	204	240	217	244	ν ₇
	-	-	304	-	(See text)
	319	336	324	340	ν ₆
(NH4) 2P	dCl4 295	K	145	к	
	т.о.	L.O.	т.о.	L.O.	
A2u	123				
	120	131	127	134	Lattice mode
	194	131 280	127 200	134 266	Lattice mode v_4
	194 -	131 280 -	127 200 295	134 266 303	Lattice mode v ₄ (See text)
Е _и	194 - 122	131 280 - 137	127 200 295 128	134 266 303 141	Lattice mode v ₄ (See text) Lattice mode
^Е и	194 - 122 163	131 280 - 137 -	127 200 295 128 178	134 266 303 141 188	Lattice mode v ₄ (See text) Lattice mode Lattice mode
^E u	194 - 122 163 204	131 280 - 137 - 241	127 200 295 128 178 211	134 266 303 141 188 241	Lattice mode v ₄ (See text) Lattice mode Lattice mode v ₇
Е _и	194 - 122 163 204	131 280 - 137 - 241 -	127 200 295 128 178 211 295	134 266 303 141 188 241 -	Lattice mode v ₄ (See text) Lattice mode Lattice mode v ₇ (See text)
^Е и	194 - 122 163 204 -	131 280 - 137 - 241 -	127 200 295 128 178 211 295 309	134 266 303 141 188 241 - -	Lattice mode v ₄ (See text) Lattice mode V ₇ (See text) (See text)

^a estimated visually K-K analysis gives 188 cm⁻¹ sh denotes a shoulder I.r. wavenumbers (cm⁻¹) for $(PtCl_{4})^{2}$ and $(PdCl_{4})^{2}$ in solution, potassium Table 7.5

and ammonium salts.

		(NH4) ^{+ b}	194	204	332
(PdCl4) ^{2⁻}		д +Х	162	178	334
	CHC1 ₃	soln. ^a	150	161	321
	((NH4,) ^{+ b}	200	204	319
$(PtCl_4)^2$		д +У	160	185	325
	CHC13	soln. ^a	147	165	313
			п) т(M-Cl)	(TD-W)§ ((TD-W)v (
			(A21	(E _u)	(E ⁿ
			۲4 ۷	۲v ۲	v6

a Goggin and Mink (1974).

b This work.

FIG. 7.0

Morphology of A2MX4 Crystals






 $v_{6}^{}(\mathrm{E_{u}})$ (in plane)

 $v_7(\mathsf{E_u})$ (in plane)









Figures 7.6-7.8

K_2 PtBr₄

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Figure	7.6	(a) (b)	A2u Eu	295 K
Figure	7.7	(c)	A _{2u}	145 K
Figure	7.8	(d)	Eu	145 K

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FIG.7.9







FIG. 7.13





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Chapter Eight

The 80 Diperiodic Groups in Three Dimensions

Introduction

A brief introduction was given in Chapter One to the 80 groups. In addition to the 230 space groups, which are used to describe structures which have periodicity in three dimensions, there are 80 diperiodic groups which can be used to describe structures which are, or approximately correspond to, planar structures. Such structures use the third dimension as a stacking direction between layers. Wood (1964) has derived these groups from the 230 space groups. Symmetry operations which are allowed in space groups may not also be allowed in the diperiodic groups owing to the loss of periodicity in the third dimension. The following symmetry operations are excluded from these groups : screw axes normal to the plane of periodicity; glide planes with glide directions out of the plane of periodicity; 'n' fold rotation axes which are not normal to the diperiodic plane; a special case for this last exclusion is where n = 2 and the axis is in the diperiodic plane, since the upper side of the plane may be like or unlike the lower side these rotations may be allowed. Mirror planes, glide planes and screw axes may lie in the diperiodic plane.

Each group may be derived from one of the five twodimensional nets (see Chapter One) in an analogous manner to which the 230 space groups are generated from the 14 Bravais lattices. These nets are indeed the two-dimensional equivalents

of the Bravais lattices. Only the rectangular net may be primitive or centred, all other nets are primitive. The 230 space groups given in "International Tables for X-ray Crystallography", hereafter called I.T.X.R.C., have sets of symmetrically equivalent sites given in terms of "Wyckoff notation", and the point symmetry of the sites given in terms of Hermann-Mauguin symbols, in addition to the number of equivalent sites. Wood has retained the notation of the sites as that of the space group from which the diperiodic group (D.G.) is derived. Each diperiodic group may be assigned a "Schonflies notation" factor group which is identical to the factor group of the corresponding space group. Table 8.1 lists the 80 groups with the full Hermann-Mauguin symbols of the group and the Schonflies symbol of the space group from which it was derived, along with the space group number as given in I.T.X.R.C. Each diperiodic group has a unique direction in the plane normal. It is found on inspection that if this direction is placed along two non-equivalent directions of certain single orthorhombic groups two non-equivalent diperiodic groups are generated; one of these may have the I.T.X.R.C. standard axis set, the other will always have a non-standard set. Both groups generated have equivalent point symmetry for their respective "Wyckoff sites". An example is given by D.G. 23 and D.G. 24, both are derived from space group 25, sites 'a' in both cases have point symmetry mm. It is important to remember that, in such cases, symmetry operations are identical but are performed on different site coordinates.

The diperiodic groups are particularly useful in dealing with "layer" structures; the confusion between diperiodic groups and space groups can be avoided by nomenclature, adopted here, of D.G. to describe a diperiodic group. It was decided to derive a set of simplified factor group analysis tables for the 80 groups. Similar tables for the 230 space groups have been derived previously (Adams and Newton 1970). Such tables would allow the irreducible representation of the structure to be given in terms of symmetry species without any lengthy calculation. All the information required is a knowledge of the symmetry of the diperiodic group adopted by the structure, and the sites occupied; such information is available from a variety of sources (e.g. Wyckoff 1968).

Calculation of Irreducible Representations

The method of Bhagavantam and Venkatarayudu (references Chapter 1) is adopted for the calculation. In outline the method entails the calculation of the atoms of the structure which are unmoved by the symmetry operations of the factor group. An atom will not be moved by a mirror plane or rotation axis if and only if the atom lies along the symmetry axis; similarly it will not be moved by an inversion centre or improper rotation if and only if the atom lies at the respective centre. Screw axes and glide planes involve translation by a fraction of the primitive translation (which are used to construct the net) and any atoms 182.

operated on do not remain invariant. Any atom on a particular site is not moved by operations of the site symmetry, but is moved by any other operations of the factor group.

It is at this stage that a simplification can be applied to the method. Sites remaining invariant for each of the 80 groups are tabulated in Table 1 at the end of the chapter. The Wyckoff notation is used for simplicity. A reducible representation may be calculated for each site using:

$$X_{j}(R) = W_{R}\Lambda_{R}$$

 $X_{j}(R)$ is the character of the jth class having symmetry operation R. W_{R} is the number of atoms invariant under operation R. Λ_{R} is the trace of the transformation matrix for operation R which is given by:

$2\cos\theta \pm 1$ where θ = the angle of rotation for operation R

+l is added for pure rotations, -l is added for rotation plus inversion. This representation is then reduced by the usual method.

$$n_1 = \frac{1}{N} \Sigma_j h_j X_i(R) X_j(R)$$
 (1)

 n_1 is the number of times the irreducible representation Γ_i is contained in the reducible representation Γ_i .

 $X_i(R)$ and $X_j(R)$ are the characters of operation R in Γ_i and Γ_j respectively. N is the order of the group (total number of symmetry elements). h_j is the number of operations in the jth class.

Another way of doing the same thing is to multiply the elements of each row of the site symmetry table for the diperiodic group (Table 1) by the number of equivalent sites in the <u>primitive</u> net, and by the contribution each makes to the representation 2Cos0±1. The reducible representations can then be reduced by:

$$n_1 = \frac{1}{N} \sum_{j=1}^{N} X_i(R) X_j(R)$$
 (2)

all symbols are as in (1).

The irreducible representation for the 3N normal modes of any structure can then be obtained by summation of the rows of table 2 for the sites occupied in the diperiodic group. In the case of the absence of a diperiodic group isomorphous with a space group, the irreducible representation may be obtained from another diperiodic group, of the same factor group, by summation of the appropriate rows which correspond to the point symmetries of the three dimensional structure.

For layer structures the only translatory modes allowed are of the acoustic type. These are easily found from the point group table of the isomorphous factor group. Layer structures have no rotational degrees of freedom; the modes calculated from Table 2 are therefore the internal modes of the layer plus the acoustic modes. In considering whether a structure is a layer structure or not it is important to inspect the distances between sets of atoms. If the distances are greater than the Van der Waal's radii for the atoms the structure may be described as a layer structure. If the inter-atomic distances are less than the Van der Waal's radii, i.e. there is interaction between them, the structure is best described by a space group and not a diperiodic group.

The use of the tables is best illustrated using examples. i) Red PbO is a layer structure comprising 1 layer per unit cell. The 3-dimensional space group for the structure is D_{4h}^5 , inspection of Table 8.1 shows that the corresponding 2-dimensional group is D.G. 63.

> Pb atoms lie on sites 2c and 0 atoms on sites 2a. Table 2 D.G.63 lists the following.

	A _{lg}	A2g	^B 1g	^B 2g	Eg	Alu	A _{2u}	Blu	B ₂ u	Eu
2c	1	0	0	0	l	0	1	0	0	1
2a	0	0	1	0	l	0	1	0	0	1
Total	1	0	1	0	2	0	2	0	0	2
ТА							1			1
Int.	1	0	1	0	2	0	1	0	0	1

TA are the acoustic translatory modes found from the point group table for D_{4h} . Int. are the internal modes of the layer.

- ii) CdCl₂ is a layer structure comprising 1 layer per unit cell. The 3-dimensional space group of the structure is D_{3d}^5 , inspection of Table 8.1 shows that there is no corresponding 2-dimensional group. Inspection shows that the <u>layer</u> symmetry is also D_{3d} . We may therefore take another D_{3d} 2-dimensional group and use this to calculate the representation, but it is important to use sites of equivalent symmetry, e.g. D.G.71 (D_{3d}^1) may be used.
 - In D_{3d}^5 CdCl₂ has Cd on sites la $\overline{3m}$. Cl on sites 2c 3m.

In D_{3d}^{1} the equivalent sites are la $\overline{3}m$. 2e 3m.

	Alg	A _{2g}	Eg	A _{lu}	A2u	Eu
la	0	0	0	0	1	1
2e	1	0	1	0	1	l
Total	1	0	1	0	2	2
TA					1	l
Int.	1	0	1	0	1	1

iii)

Red HgI₂ is a layer structure comprising 2 layers per unit cell. The 3-dimensional space group which describes the structure is D_{4h}^{15} , inspection of Table 8.1 shows no corresponding 2-dimensional group. In order to obtain the internal modes for 1 layer the symmetry of the layer must be determined, inspection shows that this is D_{2d} . Selecting D.G.57 (D_{2d}^1) .

```
In D_{4h}^{15} HgI<sub>2</sub> has Hg on sites 2a \overline{4}2m.
I on sites 4d mm.
This is for <u>2</u> layers; for <u>1</u> layer:
D_{2d}^{1} has sites la \overline{4}2m
```

```
2g mm
```

	Al	A ₂	В1	B ₂	Ε
la	0	0	0	1	l
2g ·	l	0	0	1	2
Total	1	0	0	2	3
TA				l	1
Int.	1	0	0	1	2

This agrees with the cumbersome calculation of Hiraishi (1976). The choice of a non-primitive net for vibrational analysis leads to more than the predicted number of modes. The tables have been calculated using equivalent primitive nets and automatically give the correct number of modes.

Oblique					
D.G.					
l	Pl	c_1^1	(1)	·	
2	PI	c_i^l	(2)		
3	P211	c_2^1	(3)	lst setting	
4	Pmll	C^1_s	(6)	lst setting	
5	Pbll ·	C ² s	(7)	lst setting	
6	P2/mll	c _{2h}	(10)	lst setting	
7	P2/bll	c 4 2h	(13)	lst setting	-
Rectangular			*****		
8	P112	C_2^1	(3)	2nd setting	
9	P1121	c_2^2	(4)	2nd setting	
10	C112	c ₂ ³	(5)	2nd setting	
11	Pllm	C_s^1	(6)	2nd setting	
12	Plla	C ² s	(7)	2nd setting	cba
13	Cllm	C ³ s	(8)	2nd setting	
14	P112/m	c_{2h}^{1}	(10)	2nd setting	
15	P112 ₁ /m	c_{2h}^2	(11)	2nd setting	
16	C112/m	C_{2h}^{3}	(12)	2nd setting	
17	P112/a	c ⁴ 2h	(13)	2nd setting	- cba
18	P112 ₁ /a	c_{2h}^{5}	(14)	2nd setting	cba
19	P222	1 D2	(16)		
20	P2221	D ₂ ²	(17)	bca	
21	P22121	D_2^3	(18)		
22	C222	D ₂ ⁶	(21)		
23	P2mm	C ^l ₂ v	(25)		

Table 8.1

24	Pmm2	c_{2v}^1	(25)	bca
25	Pm2 ₁ a	c_{2v}^{2}	(26)	cba
26	Pbm21	c_{2v}^2	(26)	acb
27	Pbb2	C ³ 2v	(27)	acb
28	P2ma	c _{2v}	(28)	
29	Pam2	C ⁴ 2▼	(28)	acb
30	Pab21	c ⁵ 2v	(29)	acb
31	Pnb2	c^{6}_{2v}	(30)	bca
32	Pnm21	c ⁷ 2v	(31)	acb
33	P2ba	c ⁸ 2v	(32)	
34	C2mm	C ¹¹ 2v	(35)	
35	Cmm2	c_{2v}^{14}	(38)	bca
36	Cam2	C ¹⁵ 2v	(39)	bca
37	P2/m2/m2/m	l D _{2h}	(47)	
38	P2/a2/m2/a	D_{2h}^{3}	(49)	cab
39	P2/n2/b2/a	D ₂ h	(50)	
40	P2/m2 ₁ /m2/a	D_{2h}^{5}	(51)	acb
41	P2/a21/m2/m	D_{2h}^{5}	(51)	
42	P2/n2/m2 ₁ /a	D <mark>7</mark> 2'n	(53)	acb
43	P2/a2/b21/a	D ₂ h	(54)	cab
44	P2/m21/b21/a	D <mark>9</mark> 2h	(55)	
45	P2/a21/b21/m	D _{2h}	(57)	bca
46	$P2/n2_1/m2_1/m$	D <mark>13</mark> 2h	(59)	
47	C2/m2/m2/m	D_{2h}^{19}	(65)	
48	C2/a2/m2/m	D ²¹ D _{2h}	(67)	

Square

•

49	P4	C_4^1	(75)
50	P4	S_4^1	(81)
51	P4/m	c_{4h}^1	(83)
52	P4/n	C_{4h}^3	(85)
53	P422	D_4^1	(89)
54	P4212	D_4^2	(90)
55	P4mm	C^{1}_{4v}	(99)
56	P4bm	C_{4v}^2	(100)
57	P42m	D_{2d}^{1}	(111)
58	P421m	D_{2d}^3	(113)
59	P4m2	D_{2d}^5	(115)
60	Р462	D_{2d}^7	(117)
61	P4/m2/m2/m	D_{4h}^{l}	(123)
62	P4/n2/b2/m	D_{4h}^3	(125)
63	P4/m21/b2/m	D_{4h}^{5}	(127)
64	P4/n21/m2/m	D_{4h}^{7}	(129)
Hexagonal			
65	P3	C_3^1	(143)
66	P3	Cl _{3i}	(147)
67	P312	D_3^1	(149)
68	P321	D_3^2	(150)
69	P3ml	C_{3v}^{l}	(156)
70	P31m	C_{3v}^2	(157)
71	P312/m	D ¹ 3d	(162)
72	P32/ml	D_{3d}^3	(164)
73	P6	C ₆ ¹	(168)

74	P6	c ¹ _{3h}	(174)
75	P6/m	C_{6h}^{l}	(175)
76	P622	D_6^1	(177)
77	P6mm	C ¹ _{6v}	(183)
78	P6m2	D ¹ _{3h}	(187)
79	P62m	D ³ _{3h}	(189)
80	P6/m2/m2/m	D_{6h}^{1}	(191)

m = mirror plane

2,3,4,6 = rotation axes $\overline{2}$, $\overline{3}$, $\overline{4}$, $\overline{6}$ = inversion axes 2₁ = 2 fold screw axis

a, b, n = glide planes

nomenclature relates to c a b axes respectively, e.g.

D.G.46 $P2/n2_1/m2_1/m$

2 fold axis parallel to c with diagonal glide plane normal to c.

2 fold screw axis parallel to a with mirror plane normal to a.

2 fold screw axis parallel to b with mirror plane normal to b.

D.G. 1 HO. OF POSNS 1	WYCKOFF NOTATION A 1	E		
D.G.2 NO. OF POSNS 1 1 1 1 2	WYCKOFF NOTATION A 1 C2 D3 E4 I5	E 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	i 1 1 1 0	
D.G.3 NO. OF POSNS 1 1 1 1 2	WYCKOFF NOTATION A 1 B2 C3 D4 E5	E 1 1 1 1 1	C ₂ 1 1 1 1 0	
D.G.4 NO. OF POSNS 1 2	WYCKOFF NOTATTON A 1 C2	E 1 1	0 h 1 0	

TABLE 1

D.G.5 NO. OF WYCKOFF E σ_{h} POSNS NOTATION 2 A1 10 P211 OBLIQUE

P1 OBLIQUE

P.1 OBLIQUE

Pm 11 OBLIQUE

P b11 OBLIQUE

192.

1

D.G.6 NO. OF POSNS 1 1 1 2 2 2 2 2 2 2 4	WYCKOFF NOTATION A 1 C2 D3 G4 I5 J6 K7 L8 M9 O 10	E 111111111	C ₂ 1 1 1 1 1 1 1 0 0	i 1110000000000000000000000000000000000	0 0 0 1 0	(x,y)
D.G.7 NO. OF POSNS	WYCKOFF NOTATION	[rd]	°2	i	σ _h	
2 2 2 4	A 1 D2 E3 F4 G5	1 1 1 1 1	0 0 1 1 0	1 1 0 0 0	00000	
D.G.8 NO. OF POSNS 1 1 2	WYCKOFF NOTATION A 1 C 2 E3	E 1 1	C ₂ 1 1 0			
D.G.9 NJ. OF POSNS 2	WYCKOFF NOTATION A 1	E 1	С ₂ 0			
D.G. 10 NO. OF POSNS 2 4	WYCKOFF NOTATION A 1 C2	E 1 1	°2 1 0			

P2/m11 OBLIQUE

P2/b11 OBLIQUE

P 112 RECTANGULAR

P 112 RECTANGULAR

C 112 RECTANGULAR

D.G. 11 NO. OF POSNS 1 2	WYCKOFF NOTATION A 1 B2 C3	E 1 1	0 h 1 1 0		
D.G. 12 NO. OF POSNS 2	WYCKOFF NOTATION A 1	E 1	σ _h 0		
D.G. 13 NO.OF POSNS 2 4	WYCKOFF NOTATION A 1 B2	E 1 1	o _h 1 0		
D.G. 14 NO. OF POSNS 1 1 1 2 2 2 2 2 4	WYCKOFF NOTATION A 1 B2 D3 E4 I5 J6 M7 N8 O9		C ₂ 1 1 1 1 1 1 0 0	1 1 1 0 0 0 0	0 ^h 1 1 1 1 0 0 1 1 0
D.G. 15 NO. OF POSNS 2 2 2 4	WYCKOFF NOTATION A 1 B2 E3 F4	E 1 1 1	0 0 0 0 0	i 1 0 0	o _h 0 0 1 0

P 1 1m RECTANGULAR

P 1 1a RECTANGULAR

C 1 1m RECTANGULAR

P 112/m RECTANGULAR

P 112 /m RECTANGULAR

D.G. 16 NO. OF POSNS 2 2 4 4 4 8	WYCKOFF NOTATION A 1 B2 E3 G4 I5 J6		C ₂ 1 1 0 1 0 0	i 1 1 0 0	• o [°] h 1 0 0 1 0		C 112/m RECTANGULAR
D.G. 17 NO. OF POSNS 2 2 2 4	WYCKOFF NOTATION A 1 C2 E3 G4	E 1 1 1 1	C ₂ 0 0 1 0	i 1 0 0	σ _h 0 0 0		P112/a RECTANGULAR
D.G. 18 NO. OF POSNS 2 2 4	WYCKOFF NOTATION A 1 C2 E3	E 1 1	C ₂ 0 0 0	i 1 0	o [~] h 0 0 0		P112/aRECTANGULAR
D.G. 19 NO. OF POSNS 1 1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	WYCKOFF NOTATION A 1 B2 C3 E4 I5 K6 M7 08 Q9 R 10 S 11 T 12 U 13	E 1111111111111	C ₂ (1 1 1 0 0 0 0 1 1 1	z)	C ₂ (y) 1 1 1 1 0 0 1 1 0 0 0 0 0 0 0	C ₂ (x) 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0	P222 RECTANGULAR

D. G. 20 NO. OF POSNS 2 2 2 4	WYCKOFF NOTATION A 1 B2 C3 E4	E 1 1 1	C ₂ (z) 0 0 0 0	C ₂ (y) 0 0 0 0	P222 ₁ RECTANGULAR C ₂ (x) 1 1 1 0
D.G. 21 NO. OF POSNS 2 2 4	WYCKOFF NOTATION A 1 B2 C3	E 1 1	C ₂ (z) 1 1 0	C ₂ (y) 0 0 0	$\begin{array}{c} p_{22} p_{12} \\ c_{2}(x) \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{array}$
D.G. 22 NO. OF POSNS 2 4 4 4 4 4 8	WYCKOFF NOTATION A 1 B2 E3 G4 I5 J6 K7 L8	E 1111111	C ₂ (z) 1 1 0 0 1 1 1 0	C ₂ (y) 1 1 0 1 0 0 0 0	C222 RECTANGULAR C ₂ (x) 1 1 1 0 0 0 0 0
D.G. 23 NO. OF POSNS 1 1 1 2 2 2 2 2 4	WYCKOFF NOTATION A 1 B2 C3 D4 E5 F6 G7 H8 I9		C ₂ (z) 1 1 1 1 0 0 0 0	σ _v (xz) 1 1 1 1 1 1 0 0 0	P2mm RECTANGULAR ov(yz) 1 1 1 1 0 0 1 1 0

196.
r	WYCKOFF NOTATION	E	C ₂ (z)	,σ•(xz)	σ*(yz) v	2mm2 RECTANGULAR	
	A 1	1	1	1	1		
	B2	1	1	1	1		
	E3	1	0	1	0		
	F4	1	0	1	0		
	G5	1	1	0	0		
	I6	1	0	0	0		
5					E	m2_a RECTANGULAR	
	WYCKOFF NOTATION	Е	C ₂ (z)	$\sigma_{\rm v}({\rm xz})$	$\sigma'_{v}(yz)$	1	
	A 1	1	0	0	1		
	C2	1	0	0	0		

D.G. 26					Pbm2	, RECTANGULAR
NO. OF	_ WYCKOFF	E	$C_{2}(z)$	σ(xz)	J'(yz)	
POSNS	NOTATION		2	V	V	
2	A 1	1	0	1	0	
2	B2	1	0	1	0	
4	C3	1	0	0	0	

D.G. 24

C2

1 0

0

NO. OF POSNS

1

1

2

2

2

4

D.G. 25

NO. OF

POSNS

2

4

D.G. 27 NO. OF POSNS	WYCKOFF NOTATION	Ε	C ₂ (z)	$\sigma_v(xz)$	Pbb2 σ'(yz)	RECTANGULAR
2	A 1	1	1	0	0	
2	C 2	1	1	0	0	
4	E3	1	0	0	0	

D.G. 28 NO. OF	WYCKOFF	E	$C_{o}(z)$	σ(xz)	P2ma o'(yz)	RECTANGULAR
POSNS	NOTATION		2	V	V	
2	A 1	1	1	0	0	
2	B2	1	1	0	0	
2	C3	1	0	0	1	
4	D4	1	0	0	0	

D.G. 29					Pam2	RECTANGULAR
NO. OF	WYCKOFF	Ε	$C_{o}(z)$	$\sigma(xz)$	J'(yz)	
POSNS	NOTATION		2	V	V	
2	A 1	1	1	0	0	
2	C 2	1	0	0	1	
4	D3	1	0	0	0	

D.G. 30 NO. OF POSNS	WYCKOPP NOTATION	ਣ	0 ₂ (z)	. or (xz)	Pab o'(yz)	2 TECTANGULAR
4	A 1	1	0	0	0	
D.G. 31 NO. OF POSNS 2 4	WYCKOFF NOTATION A 1 C 2	E 1 1	0 ₂ (z) 1 0	σ _v (xz) 0 0	Pnb o'(yz) 0 0	2 RECTANGULAR
D.G. 32					Pnm	2, RECTANGULAR
NO. OF POSNS	WYCKOFF NOTATION	E	C ₂ (z)	$\sigma_{V}(xz)$	$\sigma'_{V}(yz)$	
2 4	A 1 B2	1	0	0	1 0	
D.G. 33 NO. OF	WYCKOFP	Ξ	C ₂ (z)	σ _v (xz)	P2b σ'(yz)	a RECTANGULAR
2 2 4	A 1 B2 C3	1 1 1	1 1 0	0 0 0	0 0	
~ ~ ~ ~						
D.G. 34 NO. OF	WYCKOFF	Ε	C ₂ (z)	σ_v(xz)	σ'(yz) C2m	m RECTANGULAR
POSNS 2 2 4 4 4 8	NOTATION A 1 B2 C3 D4 E5 F6	1 1 1 1 1 1	1 1 0 0	1 1 0 1 0 0	1 0 0 1 0	
D.G. 35 NO. OF POSNS 2	WYCKOFF NOTATION A 1	[-] F	C ₂ (z)	σ_(xz) 1	σ'(yz) 1	m2 RECTANGULAR
4 8	D3 F4	1	1	0	1	

D.G. 36 NO. OF POSNS 4	WYCKOFF NOTATION A 1	E C ₂ 1 1	(z) . _v	(xz)	σ"(; 0	Cam: yz)	2 RECTA	ANGULAR	
4 8	D3	1 0	0		0				
D.G. 37					P2,	/m2/m	2/m RE(CTANGUL	AR
NO. OF POSNS	WYCKOFF NOTATION	EC ₂ (z) C ₂ (y)	C ₂ (x)	i	σ(xy)	$\sigma(zx)$	σ(yz)	
1	A1 B2	1 1	1	1	1	1	1	1	
1	E3	1 1	1	1	1	1	1	1	
1	F4	1 1	1	1	1	1	1	1	
2	K6	1 0	0	1	0	1	1	0	
2	M7	1 0	1	0	0	1	0	1	
2	Q9	1 1	0	0	0	0.	1	1	
2	R 10	1 1	0	0	0	0	1	1	
2	T 12	1 1	0	0	0	0	1	1	
4	U 13	1 0	0	0	0	0	0	1	
4 4	W 15	1 0	0	0	0	0	1	0	
4	X 16	1 0	0	0	0	0	1	0	
4	×18	1 0	0	0	0	0	0	0	
D.G. 38					P2,	/a2/m	2/a RE(TANGUI	AR
NO. OF POSNS	WYCKOFF NOTATION	E C ₂ (2	c) c ₂ (y)	C ₂ (x)	i	σ(ху)	o(zx)	σ(yz)	
2	A 1	1 0	0	1	1	0	0	1	
2	E3	1 1	1	1	0	0	0	0	
2	F4	1 1	1	1	0	0	0	0	
4	15 K6	1 0	1	0	0	0	0	0	
4	L7	1 1	0	0	õ	0	0	õ	
4	M8	1 0	0	1	0	0	0	0	
4	2 10	1 0	0	0	0	0	0	1	
8	R11	1 0	0	0	0	0	0	0	

D.G. 39 No. of Posns	WYCKOFF Norapton	E C ₂ (z)	c ² (3)	C ₂ (x)	i	P2/n2/ σ(xy)	62/a H o(zx)	RECTANG o(yz)	UL/R
2 2 4 4 4 4 4 4 8	A 1 B2 E3 G4 I5 K6 L7 M8	1 1 1 1 1 0 1 0 1 0 1 1 1 1 1 0	1 0 0 1 0 0	1 1 0 1 0 0 0 0 0	00100000				
D.G. 40 NO. OF POSNS	WYCKOFF	E C ₂ (z)	C ₂ (y)	C ₂ (x)	i	P2/m2 d(xy)	/m2/a o(zx)	RECTAN o(yz)	GULAR
2 2 2 4 4 4 4 4 8	A 1 C2 E3 G4 H5 I6 K7 L8	1 0 1 0 1 1 1 1 1 1 1 0 1 0 1 0	1 1 0 0 0 0		1 0 0 0 0 0 0	1 1 0 0 1 0	0 0 0 0 0 1	0 0 1 0 0 0 0	
D.G. 41 NO. OF POSNS 2 2 2 2 4 4 4 4 8	WYCKOFF NOTATION A 1 B2 E3 F4 G5 I6 J7 K8 L9	E C ₂ (z) 1 0 1 0 1 1 1 1 1 1 1 0 1 0 1 0	C ₂ (y) 1 1 0 0 1 0 0 0 0	C ₂ (x) 0 0 0 0 0 0 0 0 0 0 0	I 1 0 0 0 0 0 0 0	2/a2 o(xy) 0 0 0 0 0 0 0 0 0 0 0 0 0	/m2/m σ(zx) 1 1 1 0 1 1 0 0	RECTANG o(yz) 0 1 1 0 0 0 1 0 1 0	ULAR
D.G.42 NO. OF	WYCKOFF	в С ₂ (z) C ₂ (y)	C ₂ (x	H) j	?2/n2/m i o(xy)	$\sigma(zx)$	RECTANG) o(yz)	ULAR
2 2 4 4 8	A1 B2 E3 G4 H5 I6	1 0 1 0 1 0 1 1 1 1 1 0 1 0	0 0 0 0	1 1 0 0	1 0 0 0			0 0 0 1 0	

D.G. 43 NO. OF POSNS	WYCKOFF	E C ₂ (z)	С ₂ (у)	C ₂ (x)	P2 / i o	a2/b2 r(xy)	2 /a RE σ(zx)	CTANGUI o(yz)	AR
4 4 4 8	A 1 C2 D3 F4	1 0 1 1 1 0 1 0	0 0 0	0 0 1 0	1 0 0	0 0 0	0 0 0	0 0 0	
D.G. 44 NO. OF POSNS	WYCKOFF NOTATION	E C ₂ (z)	C ₂ (y)	C ₂ (x)	P2/m i o	12 / b2 (xy)	$\frac{1}{\sigma(zx)}$	CTANGUI o(yz)	AR
2 2 4 4 4 8	A 1 C2 E3 F4 G5 I6	1 1 1 1 1 1 1 1 1 0 1 0			1 1 0 0 0	1 0 0 1 0		0 0 0 0 0	
D.G.45 NO.OF	WYCKOFF	E C ₂ (z)	С ₂ (у)	C ₂ (x)	P2/a i c	12 / b2 r(xy)	$\frac{2}{\sigma(zx)}$ RE	CTANGUI σ(yz)	JAR
POSNS 4 4 4 8	NOTATION A 1 C 2 D3 E 4	1 0 1 1 1 0 1 0	0 0 0	0 0 0	1 0 0	0 0 0	0 0 0	0 0 1 0	
D.G. 46 NO. OF	WYCKOFF	E C ₂ (z)	C ₂ (y)	P C ₂ (x)	2/n2 i c	2/m2 (xy)	/m REC o(zx)	TANGULI o(yz)	IR
POSNS 2 2 4 4 4 8	A 1 B2 C3 E4 F5 G6	1 1 1 1 1 0 1 0 1 0 1 0			0 0 1 0 0	0 0 0 0 0	1 1 0 1 0	1 0 1 0 0	
D.G.47 NO. OF	WYCKO PF	EC _c (z)	С (у)	0 C_(x)	2/m2 i c	2/m2/n (xy)	n RECTA σ(zx)	NGULAR o(yz)	
POSNS 2 4 4 4 4 4 4 8 8 8 8 8 8 8 8 8 8 16	NOTATION A 1 B2 E3 G4 I5 K6 L7 M8 N9 O 10 P 11 R 12	2 1 1 1 1 1 0 1 0 1 0 1 0 1 0 1 0	1 1 0 0 1 0 0 0 0 0	1 1 0 1 0 0 0 0 0 0 0 0 0 0	1 1 0 0 0 0 0 0 0 0 0	1 1 1 1 0 0 0 0 1	1 1 0 1 0 1 0 1 0 1 0 0 1 0	1 0 0 1 1 1 0 0	

D.G. 48 NO. OF POSNS	WYCKOFF	B	C ₂ (z) C ₂	(y) C ₂	(x)	C2/a) i o(:	2/m2/ xy) (/m RE(o(xz)	oTANG o(yz	ULAR)
4 4 4 4 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	A 1 C 2 E 3 G 4 H 5 J 6 L 7 M 8 N 9 O 10		1 1 0 0 1 0 0 1 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0					0 0 1 1 0 0 0 0 1 0	010100100	
D.G. 49 NO. OF POSNS 1 1 2 4	WYCKOFF NOTATION A 1 B2 C3 D4	E 1111	C ₄ (z) 1 1 0 0	$C_2 C_4^3$ 1 1 1 1 1 0 0 0	i T	P4 S(QUAR	E		
D.G. 50 NO. OF POSNS 1 1 2 2 2 4	WYCKOFF NOTATION A 1 C2 E3 F4 G5 H6	E 11111	S ₄ C ₂ (1 1 1 1 0 1 0 1 0 1 0 1 0 0	z) s ₄ ³ 1 1 0 0 0		P4 S	QUAR			
D.G. 51 NO. OF POSNS 1 2 2 2 4 4 8	WYCKOFF NOTATION A 1 C2 E3 G4 H5 I6 J7 L8	E	C ₄ (z) 1 1 0 1 1 0 0 0	$C_2 C_2^3$ 1 - 1 1 - 1 1 - 1 1 - 1 1 - 1 0 - 0 0 - 0 0 - 0	i 1 1 1 1 1 0 1 0 0 0 0 0	P4/m S4 1 1 0 0 0 0 0	SQU. 0 h 1 1 0 0 1 0	ARE 5 4 1 0 0 0 0 0 0 0 0		

D.G. 52 NO. JF POSNS	WYCKOFF NOTATION	Ľ	C ₄ (z)	$c_2 c_4^3$	P4/n i S_4	SQUARE on S ₄
2 2 4 8	A 1 C 2 D 3 F 4 G 5	1 1 1 1	0 1 0 0 0 0 0	1 0 1 1 0 0 1 0 0 0	0 1 0 0 1 0 0 0 0 0	0 1 0 0 0 0 0 0 0 0
D.G. 53					P422	SQUARE
NO. OF POSNS 1 2 2 2 4 4 4 4 4 8	WYCKOFF NOTATION A 1 C2 E3 G4 H5 I6 J7 L8 O9 P 10	E 111111111	20 ₄ (z) 2 2 0 2 2 0 0 0 0 0	C ₂ (z) 1 1 1 1 1 1 0 0 0 0	20 ⁻ 2 2 2 2 0 0 0 0 1 1 0	2 2 0 0 0 0 0 1 0 0
D.G. 54					P42 ₁ 2	SQUARE
NO. OF POSNS 2 2 4 4 8	WYCHOFF NOTATION A 1 C2 D3 E4 G5	E 11111	20 ₄ (z) 0 2 0 0 0	C ₂ (z) 1 1 1 0 0	20 ¹ / ₂ 2 0 0 0 0 0 0	C ² 2 0 0 1 0
D.G. 55					P4mm S	QUARE
NO. OF POSNS 1 2 4 4 4 8	WYCKOFF NOTATION A 1 B2 C3 D4 E5 F6 G7	E 1 1 1 1 1 1 1	20 ₄ (z) 2 2 0 0 0 0 0 0	C ₂ 20 1 2 1 2 1 2 0 0 0 1 0 1 0 0	20 ⁻ v 20 ⁻ 2 2 0 1 0 0 0 0	

D.G. 56 NJ. 07 POSNS 2	WYCKOFF NOTA ION A 1	E 1	20 ₄ (2	z) ^C 2 1	20-v 0	P4om SQUARS 25 d
2 4 8	B2 C3 D4	1 1	0 0	1 - 0 0	0 0 0	2 1 0
D.G. 57 NO. OF POSNS 1	WYCKOFF NOTATION A 1 D2	E T	25 ₄ 2	C ₂ (z) 1	20'2 2	P42m SQUARE 20 2
2 2 2 4 4 4 4	E3 G4 H5 I3 L7 M8	1 1 1 1 1 1 1		1 1 1 0 0	2 0 1 1 0	2 2 2 0 0 0
4 8 D. G. 58	0 10	1	0	0	0	PA2 m SOUARE
NO. OF POSNS 2	WYCKOFF NOTATION A 1	E 1	25 ₄ 2	C ₂ (z) 1	20 <mark>2</mark> 0	$2\sigma_{d}$
4 4 8	D3 E4 F5	1 1 1	0000	1 0 0	0 0 0	0 1 0
D.G. 59 NO. OF POSNS	WYCKOFF NOTATION	E	25 ₄	C ₂ (z)	20 1	P4m2 SQUARE 20 d
1 2 2 2 4	A 1 D2 E3 F4 G5 H6	1 1 1 1 1 1	2 0 0 0	1 1 1 1 0	2 2 0 0 1	2 2 2 2 2 0

J7

K8

L9

D.G. 60 NO. OF POSNS 2 2 4 4 4 8	WYCKOFF NOTATION A 1 C2 E3 F4 G5 I6	E 11111	25 ₄ 2 0 0 0 0 0	C ₂ (2 1 1 1 1 0 0	z)	²⁰ ² 0 2 0 0 1 0	P4b2 20d 0 0 0 0 0 0 0	SQI	JARI	3	
D.G. 61 NO. OF POSNS 1 2 2 4 4 4 4 4 8 8 8 8 8 8 8 8 8 8 8 16	WYCKOFF NOTATION A 1 C 2 F 3 G 4 H 5 I 6 J 7 L 8 N 9 P 10 R 11 S 12 T 13 U 14	E 111111111111111111111111111111111111	2C ₄ (z) 2 2 0 2 2 0 2 2 0 0 0 0 0 0 0 0 0 0 0	C ₂ 1 1 1 1 1 0 0 0 0 0 0 0	20 ² 2 2 2 2 0 0 0 0 0 1 1 0 0 0 0 0	2C 2 2 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	P4/m 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	22/m ² 23 2 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	2/m 0 h 1 1 0 0 0 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0	SQU 20 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	ARE 20d 220220100010000
D.G. 62 NO. OF POSNS 2 2 4 4 4 4 8 8 8 8 8 8 16	WYCKOFF NOTATION A 1 C 2 E 3 G 4 H 5 I 6 K 7 M 8 N 9	E 11111111	20 ₄ (z) 2 0 2 0 2 0 0 0 0 0 0	C ₂ 1 1 0 1 1 0 0 0	20 ² 2 2 0 0 0 0 1 0	2012 2 0 1 0 0 1 0 0 0 0	P4/r. 0 0 1 0 0 0 0 0 0 0	2/b) 2S 0 2 0 0 0 0 0 0 0 0 0 0	2, m oh 0 0 0 0 0 0 0 0 0 0 0 0	SQUA 20 0 0 0 0 0 0 0 0 0	ARE 20 ⁻ 0 2 1 0 2 0 0 1 0

D.G. 63							P	l/m2	102	/m	SQUARE
NO. OF Posns	WYCKOFF NOTAPION	Ε	20 ₄ (z)	°: 2	202	201	i	25 ₄	σ _h 2	σ	20-d
2 2 4 4 4 8 8 8 16	A 1 D2 E3 F4 G5 I6 K7 L8	1 1 1 1 1 1 1	2 0 2 0 0 0 0	1 1 1 0 0 0 0		0 2 0 1 0 0	1 1 0 0 0 0 0 0	2 0 0 0 0 0 0	1 1 0 0 1 1 0 0	000000000000000000000000000000000000000	0 2 0 2 1 0 1 0
D.G. 64							P	∤ /n2	/m2	/m	SOUARE
NO. OF POSNS	WYCKOFF NOTATION	Ε	20 ₄ (z)	C ₂	202	201	i	25 ₄	'n	20	20-d
2 2 4 4 8 8 8 8 16	A 1 C2 D3 F4 G5 I6 J7 K8	1 1 1 1 1 1 1	0 2 0 0 0 0 0 0	1 1 0 1 0 0 0 0		20101000	0010000	2 0 0 0 0 0 0	000000000000000000000000000000000000000	22020100	0 2 1 0 0 0 1
D.G. 65 NO. OF POSNS 1 1 1 3	WYCKOFF NOTATION A 1 B2 C3 D4	E 1111	C ₃ (z) 1 1 1 0	0 1 1 1 0	2		PJ	3 HE:	XAGO	NAL	
D.G. 66 NO. OF POSMS 1 2 2 3 6	WYCKOFF NOPATION A 1 C2 D3 E4 G5	E 1111	C ₃ (z) 1 1 0 0	C 1 1 1 0 0	2 3 1 0 0 1 0	s 6 1 0 0 0	P3 S	HEX. 5 1)))	AGON	TA	

D.G. 67 NO. OF POSNE 1 1 2 2 2 2 3 6	WYCKOFF NOTATION A 1 C2 E3 G4 H5 I6 J7 L8	E 11111111	203(z) 22 22 22 22 22 20 00	. 30 <mark>2</mark> 3 3 3 0 0 0 1 0	₽3 .
D.G. 68 NC. OF POSNS 1 2 2 3 6	WYCKOFF NOTATION A 1 C2 D3 E4 G5	E 11111	203(z) 2 2 2 2 0 0	30 ¹ 2 3 0 0 1 0	P32
D.G. 69 NO. OF POSNS 1 1 1 3 6	WYCKOFF NOTATION A 1 B2 C3 D4 E5	E 1 1 1 1 1	203(z) 2 2 2 0 0	30 V 3 3 3 1 0	P3n
D.G. 70 NO. OF POSNS 1 2 3 6	WYCKOFF NOTATION A 1 B2 C3 D4	E 1111	20 ₃ (z) 2 2 0 0	30 v 3 0 1 0	P3 1r

P3 12 HEXAGONAL

P321 HEXAGONAL

P3m1 HEXAGONAL

P3 1m HEXAGONAL

D.G. 71 MO. OF POSNS	WYCKOFF NOTATION	E	²⁰ 3	301	i	25 ₆	P <u>3</u> 12/m 30d	HEXAGONAL	
1 2	A 1 C2	1	2	3	1	2	3		
3	E3 F4	1	0	1	1	0	3		
4	H5	1	2	0	0	0	0		
6	16 K7	1	0	0	0	0	1		
12	r8	1	0	0	0	0	0		
							D20/m1	TTTY A CON A T	
NO. OF	WYCKOFF	Ε	203	302	i	25 ₆	30-d	HE AAGONAL	
POSNS 1	NOTATION A 1	1	2	3	1	2	3		
2	C2	1	2	0	0	O	3		
2	D3 EA	1	2	0	0	0	3		
6	G5	1	0	1	0	0	0		
6	I6 T7	1	0	0	0	0	1		
12	01	I	0		0	0	0		
D.G. 73	WYOTAND	رتد	a	a a		a ² a	p6 HEX	AGONAL	
POSNS	NOTATION	£.	6	3	2	3	6		
1	A 1	1	1	1 1		1 1			
2	C3	1	0	0 1		0 0			
6	D4	1	0	0 0		0 0)		
D.G. 74							रजम ठेव	A GONAT.	
NO. OF	WYCKOF	F	C (2	c^2	a	- 5	5		
POSNS	NOTATION		312	3	0	h ~3	3		
1	A 1	1	1	1	1	1	1		
1	E3	1	1	1		1	1		
2	G4	1	1	1	0	0	0		
2	H5	1	1	1	0	0	0		
2	16	1	1	0	0		0		
6	L8	1	õ	0	0	0	0		

D.G. 75								I	26/1	n HI	EXA(JOM/	AL
NO. OF POSNS	WYCKOFF NOTATION	Έ	C ₆ (z)	°3	°C 2	c ²	с ⁵ 6	i	s ⁵ ₃	s ⁵ 6	σ_h	^S 6	s ₃
1	A 1	1	1	1	1	1	1	1	1	1	1	1	1
2	C 2	1	0	1	0	1	0	0	1	0	1	0	1
2	E3	1	1	1	1	1	1	0	0	0	0	0	0
3	1.4 IIE	1	0	1	0	1	0	0	0	0	1	0	0
4	п5 т6	1	0	0	1	0	0	0	0	0	0	0	0
6	J7	1	0 -	0	0	Õ	0	0	0	õ	1	0	0
12	L8	1	0	0	0	0	0	0	0	0	0	0	0
D.G. 76								P	622	HE	XAG	ONA	L
NO. OF	WYCKOFF	Ε	20	2C	2	C ₂	3C,	1	30	11			
POSNS	NOTATION		0		2	2		2		2			
1	A 1	1	2	2		1	3		3				
2	02	1	0	2		0	0		3				
2	E 3 Tr A	1	2	2		1	1		1				
Δ	H5	1	0	2		0	0		0				
6	16	1	0	0		1	0		0				
6	J7	1	0	0		0	1		0				
6	I8	1	0	0		0	0		1				
12	N9	1	0	0		0	0		0				
								-				TTOD	۸ T
NO OF	WYCKOFF	Ŧ	20	20		C	30	- 1	2000 300	m Hi 	LAA	GON	41
POSNS	NOTATION		206	20	3	2	50	V	50	d			
1	A 1	1	2	2		1	3		3				
2	B2	1	0	2		0	3		0				
3	C3	1	0	0		1	1		1				
6	D4	1	0	0		0	0		1				
6	E5	1	0	0		0	1		0				
	11.12	1	1	1 1		1 1	11		11				

D.G. 78							Р	6m2	HE	KAGOI	TAL		
NO. OF POSNS	WYCKOFE NOTATION	Ε	²⁰ 3	30	2	'n	²⁵ 3	30	V				
1 1 2 2 2 3 6 6 6 12	A 1 C2 E3 G4 H5 I6 J7 L8 N9 O 10	1 1 1 1 1 1 1 1 1	2 2 2 2 2 2 2 2 0 0 0 0		3 3 0 0 1 0 0	1 1 0 0 1 1 0 0	2 2 0 0 0 0 0 0 0						
D.G. 79 NO. OF POSNS	WYCKOFF NOTATION	E	20 ₃	3	^C 2	o_h	253 253	62m 3 c	HE:	XAGOI	NAL		
1 2 2 3 4 6 6 12	A 1 C2 E3 F4 H5 I6 J7 L8		2 2 0 2 0 0 0		3 0 1 0 0 0	1 0 1 0 0 1 0	2 2 0 0 0 0 0						
D.G. 80							P6/	m2/	m2/1	n HEI	XAG	JNAL	
NO. OF POSNS	WYCKOFF NOTATION	E	²⁰ 6	203	°2	302	3011	i	²⁵ 3	²⁵ 6	σh	30 d	30 _v
1 2 3 4 6 6 6 12 12 12 12 12 24	A 1 C2 E3 F4 H5 I6 J7 L8 N9 O 10 P 11 R 12	11111111111	2 0 0 0 0 0 0 0 0 0 0	2 2 2 0 2 0 0 0 0 0 0 0	1 1 1 1 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0	30010000000	3 3 0 1 0 0 1 0 0 0	1 0 1 0 0 0 0 0 0 0 0	2 0 0 0 0 0 0 0 0 0 0 0	2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	110100110010	3 3 1 3 1 0 1 0 1 0 0	3 3 1 0 1 0 1 0 0 0 0 0

TABLE 2 D.G. 1 C₁ WYCKOFF Α 1A 3 D.G. 2 C_i WYCKOFF Ag А ...и З 1 A-E 0 2 I 3 3 D.G. 3 °2 WYCKOFF В A 1 A-D 2 1 2 E 3 3 D.G. 4 C_s WYCKOFF A' A'' 1 A 2 1 2 C 3 3 Cs D.G. 5 WYCKOFF Α' A'' 3 3 2 A .1 c_{2h} D.G. 6 Bg B_u WYCKOFF A g A_u 1 A-G 2 0 1 0 2 2 1 1 2 I-L 2 2 M 2 1. 1 3 3 3 3

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D.G. 7 WYCKOFF 2 A-D 2 E-F 4 G	C _{2h} Ag 0 1 3	B 0 2 3	A _u 3 1 3	^B u 3 2 3	
D.G. 8 WYCKOFF 1 A-C 2 E	C ₂ A 1 3	B 2 3	·		
D.G. 9 WYCKOFF 2 A	C ₂ A 3	В З			
D.G. 10 WYCKOFF 1 A 2 C	C2 A 1 3	В 2 3			
D.G. 11 WYCKOFF 1 A-B 2 C	C s A' 2 3	<u>A</u> '' 1 3			
D.G. 12 WYCKOFF 2 A	Cs A' 3	A ' ' 3			
D.G. 13 WYCKOFF 1 A 2 B	C s A' 2 3	A'' 1 3			

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D.G. 24 WYCKOFF 1 A-B 2 E-F 2 G 4 I	C _{2v} A ₁ 1 2 2 3	A 2 0 1 1 3	^B 1 1 2 1 3	^B 2 1 1 2 3	
D.G. 25 WYCKOFF 2 A 4 C	C _{2v} A1 2 3	A2 1 3	^B 1 1 3	^B 2 2 3	
D.G. 26 WYCKOFF 2 A-B 4 C	C _{2v} A1 2 3	A_2 1 3	^B 1 1 3	^B 2 2 3	
D.G. 27 WYCKOFF 2 A-C 4 E	C _{2v} A1 1 3	A2 1 3	B 2 3	^B 2 2 3	
D.G. 28 WYCKOFF 2 A-B 2 C 4 D	C _{2v} A 1 1 2 3	A 1 1 3	^B 1 2 1 3	^B 2 2 2 3	
D.G. 29 WYCKOFF 2 A 2 C 4 D	C _{2v} A ₁ 1 2 3	A 2 1 1 3	^B 1 2 1 3	^B 2 2 2 3	
D.G. 30 WYCKOFF 4 A	C _{2v} A 1	A2 3	B 1 3	в В З	

D.G. 31 WYCKOFF 2 A 4 C	C _{2v} A ₁ 1 3	A2 1 3	^B 1 2 3	^B 2 2 3	
D.G. 32 WYCKOFF 2 A 4 B	^C 2v ^A 1 2 3	^A 2 1 3	^B 1 1 3	^B 2 2 3	
D.G. 33 WYCKOFF 2 A-B 4 C	C _{2v} 1 1 3	^А 2 1 3	^B 1 2 3	^B 2 2 3	
D.G. 34 WYCKOFF 1 A-B 2 C 2 D 2 E 4 F	C _{2v} A ₁ 1 2 2 3	A 2 0 1 1 3	^B 1 1 2 2 1 3	^B 2 1 2 1 2 3	
D.G. 35 WYCHOFF 1 A 2 C 2 D 4 F	C _{2v} A 1 1 2 3	A 2 0 1 1 3	^B 1 1 2 1 3	^B 2 1 1 2 3	
D.G. 36 WYCKOFF 2 A 2 C 4 D	C _{2v} ^A 1 1 2 3	A 2 1 1 3	^B 1 2 2 3	B ₂ 2 1 3	

D.G. 37 WYCKOFF 1 A-F 2 I-K 2 M-O 2 Q-T 4 U-V 4 W-X 4 W-X 4 Y 8 X	D _{2h} A _g 0 1 1 2 2 3	^B 1g 0 1 1 0 1 1 2 3	^B 2g 0 1 0 1 1 2 1 3	B ₃ g 0 1 1 2 1 3	A _u 0 0 0 1 1 3	^B Tu 1 1 1 2 2 1 3	^B 2u 1 1 1 2 1 2 3	^B 3u 1 1 1 1 2 2 3			
D.G. 38 WYCKOFF 2 A-D 2 E.F 4 I 4 K-L 4 M-P 4 Q 8 R	D _{2h} A _g 0 1 1 2 3	^B 1g 0 1 2 2 1 2 3	^B 2g 0 1 2 1 2 1 3	^B 3g 0 1 2 2 1 3	A _u 1 0 1 1 1 3	^B 1u 1 2 2 1 3	^B 2u 2 1 2 1 2 3	^B 3u 2 1 2 2 2 3		•	
D.G. 39 WYCKOFF 2 A-B 4 E 4 G 4 J 4 K-L 8 M	D _{2h} A _g 0 1 1 3	^B 1g 1 0 2 2 1 3	^B 2g 1 0 2 1 2 3	^B 3g 1 0 1 2 2 3	A _u 0 3 1 1 3	^B 1u 1 3 2 2 1 3	^B 2u 1 3 2 1 2 3	^B 3u 1 3 1 2 3	• •		
D.G. 40 WYCKOFF 2 A-C 2 E 4 G-H 4 I 4 K 8 L	D _{2h} A _g 0 1 1 2 2 3	^B 1g 0 2 1 3	^B 2g 0 1 1 2 1 3	^B 3g 0 1 2 1 2 3	A _u 1 0 1 1 1 3	^B 1u 2 1 2 2 2 3	^B 2u 1 1 1 2 3	B _{3u} 2 1 2 2 1 3			

D.G. 41 WYCKOFF 2 A-B 2 E-F 4 G 4 I-J 4 K 8 L	D _{2h} A 0 1 2 2 3	^B 1g 0 2 1 3	^B 2g 0 1 1 2 1 3	^B 3g 0 1 2 1 2 3	A _u 1 0 1 1 3	^B 1u 2 1 2 2 2 3	^B 2u 1 1 1 2 3	^B 3u 2 1 2 2 1 3		·
D.G. 42 WYCKOFF 2 A-B 4 E 4 G 4 H 8 I	D A g 0 1 2 3	^B 1g 0 2 2 1 3	^B 2g 0 2 1 3	^B 3g 0 1 2 2 3	Au 1 1 1 3	^B 1u 2 2 2 2 3	^B 2u 2 2 1 2 3	^B 3u 1 1 2 1 3	·	
D.G. 43 WYCKOFF 4 A 4 C 4 D 8 F	D _{2h} A _g 0 1 1 3	^B 1g 0 2 1 3	^B 2g 0 1 2 3	^B 3g 0 2 2 3	Au 3 1 1 3	^B 1u 3 2 1 3	^B 2u 3 1 2 3	^B 3u 3 2 2 3		
D.G. 44 WYCKOFF 2 A-C 4 E-F 4 G 8 I	D _{2h} A _g 0 1 2 3	^B 1g 0 1 2 3	^B 2g 0 2 1 3	^B 3g 0 2 1 3	A _u 1 1 3	^B 1u 1 1 3	^B 2u 2 2 3	^B 3u 2 2 3		
D.G. 45 WYCKOFF 4 A 4 C 4 D 8 E	D _{2h} Ag 0 1 2 3	^B 1g 0 2 2 3	^B 2g 0 2 1 3	^B 3g 0 1 1 3	A _u 3 1 1 3	^B 1u 3 2 1 3	^B 2u 3 2 2 3	^B 3u 3 1 2 3		

D.G. 46	D _{2h}							
WYCKOFF	Ag	B 1g	B 2g	^в . Зд	A u	^B 1u	^B 2u	^B 3u
2 A-B	1	0	1	1	0	1	1	1
4 C	0	0	0	0	3	3	3	3
4 E	2	1	1	2	1	2	2	1
4 F	2	1	2	1	1	2	1	2
8 G	3	3	3	3	3	3	3	3
D.G. 47	D _{2h}							

WYCKOFF	Ag	^B 1g	B _{2g}	B 3g	Au	^B 1u	^B 2u	^B 3u
1 A–B	0	0	0	0	0	1	1	1
2 E	0	0	0	0	1	1	2	2
2 G	1	1	1	0	0	1	1	1
2 I	1	1	0	1	0	1	1	1
2 K-L	1	0	1	1	0	1	1	1
4 M	1	1	2	2	1	1	2	2
4 N	2	1	1	2	1	2	2	1
4 0	2	1	2	1	1	2	1	2
4 P	2	2	1	1	1	1	2	2
8 R	3	3	3	3	3	3	3	3

D.G. 48	$^{ m D}$ 2h							
WYCKOFF	Ag	^B 1g	^B 2g	B 3g	Au	^B 1u	^B 2u	^B 3u
2 A	0	1	1	1	0	1	1	1
2 C	0	0 .	0	0	1	2	2	1
2 E	0	0	0	0	1	2	• 1	2
2 G .	1	0	1	1	0	1	1	1
4 H	1	2	2	1	1	2	2	1
4 J	1	2	1	2	1	2	1	2
4 L	1	1	2	2	1	1	2	2
4 M	2	1	1	2	1	2	2	1
4 N	2	1	2	1	1	2	1	2
8 0	3	3	3	3	3	3	3	3

D.G. 49 WYCKOFF 1 A-B 2 C 4 D	C ₄ A B E 1 O 1 1 1 2 3 3 3	
D.G. 50 WYCKOFF 1 A-C 2 E-G 4 H	S ₄ A B E O O 1 1 1 2 3 3 3	
D.G. 51 WYCKOFF 1 A-C 2 E 2 G-H 4 I 4 J 8 L	$\begin{array}{c} {}^{C}_{4h} \\ {}^{A}_{g} {}^{B}_{g} {}^{E}_{g} {}^{A}_{u} {}^{B}_{u} {}^{E}_{u} \\ {}^{C}_{0} {}^{O}_{0} {}^{1}_{1} {}^{O}_{1} \\ {}^{O}_{0} {}^{O}_{0} {}^{1}_{1} {}^{1}_{2} \\ {}^{1}_{1} {}^{O}_{1} {}^{1}_{1} {}^{1}_{2} \\ {}^{1}_{2} {}^{2}_{2} {}^{1}_{1} {}^{1}_{1} \\ {}^{2}_{2} {}^{2}_{2} {}^{1}_{1} {}^{1}_{1} \\ {}^{2}_{3} {}^{3}_{3} \\ {}^{3}_{3} {}^{3}_{3} \\ {}^{3}_{3} \\ {}^{3}_{3} \\ {}^{S}_{3} \\ {}$	
D.G. 52 WYCKOFF 2 A 2 C 4 D 4 F 8 G	$\begin{array}{c} {}^{C}_{4h} \\ {}^{A}_{g} {}^{B}_{g} {}^{E}_{g} {}^{A}_{u} {}^{B}_{u} {}^{E}_{u} \\ 0 & 1 & 1 & 1 & 0 & 1 \\ 1 & 0 & 1 & 1 & 0 & 1 \\ 1 & 0 & 1 & 1 & 0 & 1 \\ 0 & 0 & 0 & 3 & 3 & 3 \\ 1 & 1 & 2 & 1 & 1 & 2 \\ 3 & 3 & 3 & 3 & 3 & 3 \end{array}$	
D.G. 53 WYCKQFF 1 A-C 2 E 2 G-H 4 I 4 J 4 L-O 8 P	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	

D.G. 54 WYCKOFF 2 A 2 C 4 D 4 E 8 G	D ₄ A ₁ 0 1 1 3	A ₂ 1 1 2 3	B 1 1 0 1 2 3	E ₂ 0 1 1 3	E 2 4 3 6
D.G. 55 WYCKOFF 1 A-B 2 C 4 D 4 E-F 8 G	C _{4v} A 1 1 2 2 3	A2 0 0 1 1 3	^B 1 0 1 2 3	^B 2 0 2 1 3	E 1 2 3 6
D.G. 56 WYCKOFF 2 A 2 B 4 C 8 D	C _{4v} A1 1 2 3	A2 1 0 1 3	^B 1 0 1 3	B ₂ 0 1 2 3	E 2 3 6
D.G. 57 WYCKOFF 1 A-D 2 E 2 G-H 4 I-L 4 M 4 N 8 O	D _{2d} A 1 0 1 1 2 3	A ₂ 0 1 0 2 1 1 3	B 0 0 1 1 3	^B 2 1 1 2 3	E 1 2 3 4 3 6
D.G. 58 WYCKOFF 2 A 2 C 4 D 4 E 8 F	D ₂₀ A 1 0 1 2 3	A 0 0 1 1 3	^B 1 0 1 1 3	^B 2 1 1 2 3	E 2 4 3 6

D.G. 61	D 4h									
MACKOL E	A 1g	A _{2g}	B 1g	B _{2g}	Eg	A Iu	A 2u	^B 1u	^B 2u	Eu
1 A-C	0	0	0	0	൦ഁ	0	1	0	0	1
2 F	0	0	0	0	0	0	1	0	1	2
2 G-H	1	0	0	0	1	0	1	Θ	0	1
4 I	1	0	1	0	2	0	1	0	1	2
4 J	1	1	1	1	1	0	1	1	0	2
4 L-N	1	1	1	1	1	0	1	0	1	2
8 P 8 D	2	2	2	2	2	1	7	1	1	4
0 H 8 c m	2	1	1	2 1	3	1	2	2	1	3
0 5- <u>r</u> 16 TI	2	ו 2	2	2	5	2	2	ו כ	2	5
	1	2	U		-	U	2			-
D.G. 62	^D 4h									
WYCKOFF	A 1g	A _{2g}	B 1g	B _{2g}	Eg	A _{1u}	A 2u	^B 1u	^B 2u	Eu
2 A	0	1	0	0	1	0	1	0	0	1
2 C	0	0	0	1	1	0	1	0	0	1
4 E	0	0	0	0	0	1	2	2	1	3
4 G	1	1	0	0	2	1	1	0	0	2
4 H 9 T	1	0	0	7	2	0	1	1	0	2
	1	2	2	1	3	1	2	2	1	3
	1	۲ ۲	1	2	ა ა	1	2	2	2	ر د
16 N	2	3	3	2 3	5 6	3	2 3	2 3	3	5 6

2 4 3 6 3

•	D.G. 63 WYCKOFF 2 A 2 D 4 E 4 F 4 F 4 G 8 I 8 K 16 L	D _{4h} A 1g O 1 1 2 2 3	A _{2g} 0 1 0 1 2 1 3	^B 1g 0 0 0 1 2 1 3	^B 2g 0 0 1 1 2 3	Eg 0 2 2 1 2 3 6	A 1u 1 0 1 0 0 1 1 3	A2u 1 1 1 1 1 2 3	^B 1u 0 1 0 1 1 2 3	^B 2u 0 0 0 0 1 1 3	Eu 2 2 2 2 2 2 4 3 6
	D. G. 64 WYCKOFF 2 A 2 C 4 D 4 F 8 G 8 I 8 J 16 K	D _{4h} A 1g 0 1 0 1 2 2 3	[▲] 2g 0 0 0 2 1 1 3	^B 1g 1 0 1 2 2 1 3	^B 2g 0 0 0 1 1 2 3	Eg 1 1 0 2 3 3 6	A 1u 0 1 0 1 1 1 3	A ₂ u 1 2 1 2 2 2 3	^B 1u 0 2 0 2 1 2 3	^B 2u 0 1 1 2 1 3	Eu 1 1 3 2 3 3 3 6
	D.G. 65 WYCKOFF 1 A-C 3 D	C ₃ A 1 3	E 1 3								
	D.G. 66 WYCKOFF 1 A 2 C-D 3 E 6 G	C _{3i} A _g 0 1 0 3	(s ₆) Eg 0 1 0 3	A _u 1 1 3 3	Eu 1 1 3 3						
	D.G. 67 WYCKOFF 1 A-E 2 G-I 3 J 6 L	D ₃ A ₁ 0 1 3	A2 1 1 2 3	E 1 2 3 6							

D.G. 68 WYCKOFF 1 A 2 C-D 3 E 6 G	D ₃ A ₁ 0 1 3	A2 1 1 2 3	E 1 2 3 6							
D.G. 69 WYCKOFF 1 A-C 3 D 6 E	C _{3v} A ₁ 1 2 3	A2 0 1 3	E 1 3 6		·			•		
D.G. 70 WYCKOFF 1 A 2 B 3 C 6 D	C _{3⊽} Å1 1 2 3	▲ ₂ 0 1 3	E 1 2 3 6	·			·		•	• •
D.G. 71 WYCKOFF 1 A 2 C 2 E 3 F 4 H 6 I 6 K 12 L	D ₃ d A 1g O O 1 0 1 2 3.	A ² g 0 1 0 1 2 1 3	Eg 0 1 1 0 2 3 3 6	A 1u 0 0 1 1 1 3	A _{2u} 1 1 2 1 2 3	Eu 1 1 3 2 3 6				
D.G. 72 WYCKOFF 1 A 2 C-D 3 E 6 G 6 I 12 J	D ₃ d A _{1g} 0 1 0 1 2 3	A _{2g} 0 0 2 1 3	E g 0 1 0 3 3 6	A 1u 0 1 1 3	A 20 1 1 2 2 3	Eu 1 3 3 6				

D.G. 73 WYCKOFF 1 A 2 B 3 C 6 D	C ₆ A 1 1 3	B 0 1 2 3	E 1 1 2 3	E ₂ 0 1 1 3				
D.G. 74 WYCKOFF 1 A-E 2 G-I 3 J 6 L	C _{3h} A' 0 1 2 3	E' 1 1 2 3	A'' 1 1 3	E'' O 1 1 3				
D.G. 75 WYCKOFF 1 A 2 C 2 E 3 F 4 H 6 I 6 J 12 L	C _{6h} A _g 0 1 0 1 2 3	Bg 0 1 0 1 2 1 3	E 1g 0 1 0 1 2 1 3	E 2g 0 1 0 0 1 1 2 3	A _u 1 1 1 1 1 1 3	Bu 0 0 2 1 2 3	E lu 1 1 2 1 2 3	E _{2u} 0 0 1 1 1 3
D.G. 76 WYCKOFF 1 A 2 C 2 E 2 F 4 H 6 I 6 J 6 L 12 N	D ₆ A ₁ 0 1 0 1 1 1 3	A 2 1 1 1 1 1 2 2 3	^B 1 0 1 0 1 2 1 2 3	B2 0 0 1 1 2 1 3	E 1 1 2 2 4 3 6	E 2 0 1 0 1 2 2 3 3 6		
D.G. 77 WYCKOFF 1 A 2 B 3 C 6 D 6 E	C 6v A 1 1 1 2 2	A 2 0 0 1	^B 1 0 1 1 2 2	B2 0 1 21	E 1 1 2 336			

D.G. 78	ם 31	า				
WYCKO PP	A 1	A'2	ΞĽ	A''	A''	Ξ!!
1 A- E 2 G-I 3 J 6 L 6 N 12 O	0 1 2 2 3	0 0 1 2 1 3	1 2 4 3 6	0 0 1 1 3	1 1 1 2 3	0 1 2 3 6
D.G. 79	Dah					
WYCKOFF	A'1	A'2	Ε'	A''	A''	Ξ''
1 A 2 C 2 E 3 F 4 H 6 I	0 0 1 1 2	0 0 1 1	1 2 1 2 2 3	0 1 0 1 1	1 1 1 1 2	0 0 1 2 3
6 J 10 T	2	2	4	1	1	2

D.G. 80	D _{6h}		·									
MAGKOLE	A 1g	A 2g	B 1g	B _{2g}	E 1g	E _{2g}	A 1u	A 2u	B 1u	^B 2u	E 1u	^E 2u
1 A	0	0	0	0	0	0	0	1 -	0	0	1	0
2 C	0	0	1	0	0	1	С	1	0	0	1	0
2 E	1	Ú	0	0	1	0	0	1	0	0	1	0
3 F	0	0	0	0	0	0	0	1	1	1	2	1
4 H	1	0	1	Ó	1	1	0	1	0	1	1	1
6 I	1	0	1	1	2	1	0	1	1	1	2	1
б Ј	1	1	0	1	1	2	0	1	1	1	2	1
6 Г	1	1	1	0	1	2	0	1	1	1	2	1
12 N	2	1	1	2	3	3	1	2	2	1	3	3
12 0	2	1	2	1	3	3	1	2	1	2	3	3
12 P	2	2	1	1	2	4	1	1	2	2 .	4	2
24 R	3	3	3	3	6	6	3	3	3	3	6	6

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Appendix 1

Kramers-Kronig analysis program.

P2065AM_ECH0E1 (INPUT,OUTPUT,TAPE1,TAPE5=INPUT,TAPE6=OUTPUT) COMMON A1(00),G1(-00),C1(+00),E1(+00),F1(-00), 2P,G10,E2,E2,N,MM,02,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN DIMESEION 01(00) INTEGEP 0,0,Q0,K,RE,M,MM,MN,K P1=3,1a,1525b38 TV=1,000/P1 THIS 15 TO S55VE AS A CHECK ON VALUES OF OBSECVED DATA_ONLY THIS 15 TO S55VE AS A CHECK ON VALUES CALCULATED FROM "ECH0ES" AND "ECH0E2" ALL SYMPOLS APE THE SAME AS IN ECH0ES OSCILLATOR DENDETED NOT DE SUPPL IED ND CUEVE FIT IS INCOEPORATED VALUES ARE CALCULATED DIFECT FROM N,MM,31(1), A1(1),R,Q, 1 READ(5,100)N,MM WRITE(6,292)N,MM C22 FORMT1(14,NO OF POINTS=,I5,2X,20H_NO OF OSCILLATORS=,I5) N=NO OF PINTS IN SECTRUM MENO OF OSCILLATORS FREADUENCIES REQUISED: (READ(1,101) (11),I=1,N) S FORMT1(14 HAVELEVSTHS TAKEN=,5(2X,F12,6)) (READ(2,101) (3) (41(1),I=1,N) 30 FORMT1(24,DEFTEDINTES, TAKEN=,5(2X,F12,6)) (READ(5,101) (3) (41(1),I=1,N) 30 FORMT1(14,O,0,I) 30 FORMT1(14,O,1,I) 31 F 0000000 00 C FORMAT(4H QQ=,15) RR=R+1 WRITE(2,651)RR CALL GRAPHID(1,A1) D0 501 I=1,N A1(I)=A1(I)/100.000 C1(I)=ALOG(SQPT(A1(I))) C0'ITINUE FORMAT(4H RR=,I5) FORMAT(2I5) FORMAT(IT) FORMAT(I 501 651 100 105 107 101

229.

SUBSONTING KKOVGLE(01) SUBSONTING KKOVGLE(01) 101(11), 41(10), 74(10), 74(100), 74(100), 74(100), 74(100), 101(11), 74(10), 74(10), 74(100), 74(100), 74(100), 74(100), 74(100), 11, 74(100), 74(100), 74(100), 74(100), 74(100), 74(100), 74(100), 74(100), 11, 74(100), 74(100), 74(100), 74(100), 74(100), 74(100), 74(100), 74(100), 11, 74(100), 74(100 000 C С C С С C 00 CALL GRAPHIC(-1,Y1) CALL GRAPHIC(0,G1) CALL GRAPHIC(0,H1) CALL GRAPHIC(0,H1) CALL GRAPHIC(0,Q1) RETURN END

SUBPOUTINE CLADIS(01) COMMON A1(:00),B1(-00),C1(400),E1(400),F1(400), 1V1(11),W1(15),Z1(11),T(400),A2(00),C2(400), 2P,0,00,R,R²,N,MM,PI,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN DIMENSION D1(400) INTESER P,0,00,R,RE,M,MM,MN,K CALCULATE INTEGRAL FROM KRAMERS KRONIG OUTPUT SPECTRA E=0.000 D0 20 I=00,RR P=I+1 IF(P.GT.RR)G0 TO 20 A=01(I)/B1(I) B=31(P)/B1(I) D=V*(C*A+C*3) E=E+D C D=V*(C*A+C*B) E=E+D T(I)=E CONTINUE WRITE(5,203) (T(I),I=QQ,RR) FORMAT(20H THE KK OSC. STRENGTH V1=,5(2X,F10.4)) RETURN END 20 LHU SUBROUTINE GRAPHIC(MN,D1) COMMON A1(200),B1(200),C1(200),E1(200),F1(200), 1V1(15),M1(15),T1(10),A2(460),C2(400), 2P1(1)(0,E,E,1),T1(10),A2(460),C2(400), 2P1(1)(0,E,E,1),T1(10),A2(460),C2(400), DATA FOR DL DTE2 P1(1)(1,E,E,1),T1(1),T2(2,XX,FN,W1,M,K,YNAX,YMIN) DATA FOR DL DTE2 TARES MVELENCTHS,AND VARIABLES, FINDS MAX AND MIN AND ADJUSTS VALUES ACCORDINGLY TO GIVE APBITRARY UNITS WHEN MN=0,-1 TARES MVELENCTHS,AND VARIABLES, FINDS MAX AND MIN AND ADJUSTS VALUES ACCORDINGLY TO GIVE APBITRARY UNITS WHEN MN=0,-1 WHEN MN=1 MD SCALING VALUES ARE PLOTTED AS CALCULATED K= NUTHER OF SETS OF DATA M= NUTHER OF SUTPUT PDIMTS FW= FINAL WARUNUBEF WI=81(20) WSTTE(1,31)FW.WI.M.K W2TTE(1,31)FW.WI.M.K W2TTE(1,30)FW.K GO TO 10 100 CONTINUE GO TO 31 100 YMXE:0 100 CONTINUE GO TO 32 100 YMXE:0 100 Y 203 0000000000

Appendix 2

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Simple harmonic oscillator program (for Transverse Optic mode analysis)
292 298 293 102 10 9 30: R=N-3 WRITE(8,303)R FORMAT(11H S.O.L.F.=,15) WRITE(5,303)P Gei WRITE(5,30.)Q WRITE(5,30.)Q WRITE(5,50)QQ 0 FORMAT(13H CONTROL NO=,I5) Q0=0+1 WRITE(5,50)QQ 0 FORMAT(4H Q0=,I5) RR=R=1 WRITE(5,60)PR CALL GRAPHIC(1,A1) D0 501 I=1,N A1(T)=A1(T)/100.000 G1(T)=ALOG(SQRT(A1(I))) 1 CONTINUE CALL CURVE CALL CURVE 1 FORMAT(314 THE OSCILLATOR PARAMETERS ARE,2X, 119H EPSILO'I INFINITY=,F3.1) 1 FORMAT(314 THE OSCILLATOR PARAMETERS ARE,2X, 119H EPSILO'I INFINITY=,F3.1) 1 FORMAT(114 OSC. STEPHGTH=,F10.1,2X,10H EST. FREQUENCY=,F10.3, 11cH D2MP. CONSTANT=,F10.4) 3 FORMAT(3F10.0) CALL CURVE(01) CAL 303 304 E50 501 651 100 101 200 201 103 END

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C

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С

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SUBCOUTINE CLASOSC C0440M A1 (400),B1(400),C1(400),E1(400),F1(400), 1V1(15),M1(15),Z1(15),T1(400),Z2(400),C2(400), 2P,10,00,R,RE,N+MM,T,V,VV,YY,ZY,XY,FN+MI,M+K,YMAX,YMIN INTEGES P.0,0,0,R,RE,HIN,YN+K FITS SUBCOUTINE IS VCEV IMPORTANT, REFLECTIVITY VALUES ARE CALCULATED USING OSCILLATOR PARAMETERS SUPPLIED AT AUTOMATIC CURVE FITTING ROUTINE AND THE DIFFERENCE HINIMISED THESE VALUES ASE THEN SUPPLIED TO SUBROUTINE (KCVCLE THE DEST INITIAL GUESS DECREASES COMPUTER TIME B at(1)*31(1) G = 0.000 D = 1, 1 = 1, N B = 31(1)*31(1) G = 0.000 D = 1, 10 = 1, NM C = 0.000 D = 1, 10 = 1, NM C = 0.000 D = 1, 10 = 1, NM D = 1, 10 = 0, 10 = 1, NM D = 1, 10 = 0, 10 = 1, NM D = 1, 10 = 0, 10 = 1, NM C = 0, 10 = 1, NM D = 1, 10 = 0, 10 = 1, NM D = 1, 10 = 0, 10 = 1, NM C = 0, 10 = 0, 10 = 1, NM D = 1, 10 = 0, 10 = 1, 10, 10 = 1, 1 00000 С 701 702

A

SUBSOUTIONE KKKYCLE(01) (01107) At(00);/d1(00);01(100);02(100);02(100); 100107) At(00);/d1(00);02(100);00(100);01(100);01(100);01(100); 11000;/d100);02(100);00(100);00(100);01(100);01(100);01(100); 11000;/d100);02(100);00(100);00(100);00(100);01(100);01(100); 11000;/d100;/d100);00(100);00(100);00(100);01(100);01(100);01(100); 11000;/d1 000 С С С С С С CC С CALL GRAPHIC(-1,X1) CALL GRAPHIC(-1,Y1) CALL GRAPHIC(0,G1) CALL GRAPHIC(0,G1) CALL GRAPHIC(0,G1) RETURN END

SUBROUTINE CLADIS(01) COMMON A1(-00),E1(-00),C1(-00),E1(-00),F1(-00), 1V1(17),W1(15),Z1(17),T(-00),A2(-00),C2(-00), 2P,0,00,R,20,N,MM,PI,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN DITENSION 01(-00) INTESER P,0,00,R,20,M,MM,MN,K CALCULTE INTEGRAL FROM KRAMERS KRONIG OUTPUT SPECTRA E=0.000 D0 20 I=00,RR P=I+1 IF(P.GT.RE)GO TO 20 A=01(I)/01(I) D=V*(C*A+C*B) E=E+0 T(I)=E CONTINUE WRITE(2,203) (T(I),I=00,RR) FORMAT(26H THE KK OSC. STRENGTH V1=,5(2X,F10.4)) RETURN END С 20 203 END SUBROUTINE GRAPHIC(MN,D1) COMMON A1('00),81('00),C1(400),E1(400),F1(400), 1V1(15),W1(15),Z1(1F),T(400),A2(400),C2(400), 2P,Q,QQ,R,RR,N,MM,PI,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN DIMENSION D1(400) INTESER P,QQR,R,RR,M,MM,MN,K DATA FOR PLOTTE? TAKES WAVELENGTHS,AND VARIABLES, FINDS MAX AND MIN AND ADJUSTS VALUES ACCORDINGLY TO GIVE ARBITRARY UNITS WHEN MN=0 WHEN MN=1 NC SCALING VALUES ARE PLOTTED AS CALCULATED K= NUMBER OF SETS OF DATA H= MUMBER OF OUTPUT POINTS FA= FINAL WAVENUMBER WI= INITIAL WAVENUMBER K=3 0000000000 HUBBER OF OUTPUT POINTS = FINAL WAVENUMBER K=6 M=(R2-QQ)+1 FW=B1(QQ) WI=B1(QQ) WRITE(1,31)FW,WI,M,K WRITE(1,31)FW,WI,M,K WRITE(1,31)FW,WI,M,K WRITE(1,31)FW,WI,M,K WRITE(1,31)FW,WI,M,K WRITE(1,31)FW,WI,M,K WRITE(1,31)FW,WI,M,K WRITE(1,31)FW,WI,M,K WRITE(1,30) G01(1,5,7,7) MAX=0,0 YMAX=0.0 YMAX=0.0 YMIN=0.0 GO TO 400 YMIN=0.1 GO TO 400 YMIN=0.1 GO TO 400 YMIN=0.1 GO TO 400 YMIN=0.2 DO 400 I=QQ,RR IF (01(I).LT.YMIN) GO TO 502 IF (01(I).LT.YMIN) GO TO 502 IF (01(I).ST.YMAX) GO TO 502 IF (01(I).ST.YMAX) GO TO 503 GO TO 501 YMAX=01(I) GONTINUE OO 403 I=QQ,RR D1(I)=(D1(I)-YMIN)*100.00/(YMAX-YMIN) CONTINUE WRITE(1,30) (01(I),I=0Q,RR) FOXMAT(EF0.3) FOXMAT(F0.02X,F4.0,2X,I3,2X,I2,60X) RETURN END 40+ 401 402 400 500 502 503 501 1 403 405 30 31

SUBSOUTINE CURVE CONNON A1 (00) 61 (00) C1(00) F1 (00) F1 (00) , 2P, (, 20, 2, 2, 1, 10, P, P, V, VY, YZ, XX, FN, WI, M, K, YMAX, YMIN INTERSIDE A1, 10, FN, ET, HONIT UTTENSIDE V (1, 6) G (.6) HESL (1037), HESD (-6), DELTA(-6), H(323) HIS SOUTINE SETS UP CUPVE FIT USTIN PHISS CONTINUES TO POWER FIT USTINE CANDING SOUTINE CONCEPTING STORAL WAST INTO POWER FIT USTINE CLASS TO UTTO AVAILABLE CONCEPNING NOTIFIES IN A TIFEARITUE WETHOD WININGSATION IS DOWE AY LEAST SOUAPES METHOD PHISS IS AN ITTERATIVE WETHOD WININGSATION IS DOWE AY LEAST SOUAPES METHOD NOTIFIES IS AN UTERATIVE WETHOD WININGSATION IS DOWE AY LEAST SOUAPES METHOD PHISS IS AN UTERATIVE WETHOD WININGSATION IS DOWE AY LEAST SOUAPES METHOD NOTIFIES IS AN UTERATIVE WETHOD WININGSATION IS DOWE AY LEAST SOUAPES METHOD NOTIFIES IS AN UTERATIVE WETHOD WININGSATION AVAILABLE CONCEPNING NOTIFIES IN MASSIMUM AND INFORMATION AVAILABLE CONCEPNING NOTIFIES IN A WASTER VALUES IN X HIERMAIL M2EMMAIL NOTHING THE CONCEPNING Y (41) = Y11 J/ 1000.0 X (H1+J) = X1 (J) Y (41) = Y11 J/ 1000.0 X (H1+J) = X1 (J) Y (41) = Y11 J/ 1000.0 X (H1+J) = X1 (J) Y (41) = Y1 (J) (51) = 1.M3 WETTE C: 100) F WETTER C: 100 F WET 0000000 0 С C

0	10 C4 C4 20	SUBROUTINE FUNCT(M3,X,F) COMMON A1(500),B1(500),C1(400),E1(400),F1(400), 1V1(15),W1(15),Z1(1),T(400),A2(400),C2(400), 2P,Q,QQ,R,R,N,MM,PT,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN INTEGER P,Q,QQ,R,RR DIMENSION X(M3) ET CURRENT PARAMETER VALUES INTO XX,V1,W1,Z1 M1=MM+1 M2=MM+41 00 10 J=1,AM V1(J)=X(J+1)*1000.0 W1(J)=X(M1+J) Z1(J)=X(M1+J) Z1(J)=X(M1+J) CONTINUE XX=X(1) NLCULATE ARRAY C2 CALL CLASOSC ALCULATE ERROR FUNCTION TO BE MINIMIZED F=0.0 D0 20 I=1,N F=F+(C1(T)-C2(I))**2 RETURN END
C	C4 10	SUBROUTINE FUNSET(M3, X, STEP, FVEC) DIMENSION X (M3), STEP(M3), FVEC(M3) LCULATES FUNCTION VALUES SO THAT DERIVATIVES MAY BE ESTIMATED DO 10 I=1,M3 Y=X(I) X(I)=Y+STEP(I) CALL FUNCT(M3,X,Z) FVEC(I)=Z X(I)=Y CONTINUE RETURN END
C	мэн	SUBROUTINE MONIT(M3,X,F,G,HESL,IL,HESD,IFC) DIMENSION X(M3),G(M3),HESL(IL),HESD(M3) NITORING SUBROUTINE IF(IFC.LT.A)GOTO10 WRITE(5,100)IFC,F WRITE(5,120)(X(I),I=1,M3)
	10 100 110 120 130	<pre>Reform CONTINUE WRITE(5,110) WRITE(5,120) (X(I),I=1,M3) WRITE(5,120) (X(I),I=1,M3) WRITE(5,120) (G(I),I=1,M3) Refurn Format(13H NO OF EVALS=,I3,16H FUNCTION VALUE=,E20.10) Format(13H SPADIENT VECTOR,/(10E12.4))</pre>

Appendix 3

Simple harmonic oscillator program

(for Transverse and Longitudinal Optic mode

analysis)

PSOGRAM ECHOE2 (INPUT, OUTPUT, TAPE1, TAPE5= INPUT, TAPE6=OUTPUT) COMMON A1(400), d1(400), c1(400), c1(400), c1(400), 2P,0,00, R, RF, N, MM, PI,V,VV, YY,ZZ,XX,FW, WI,M,K,YMAX,YMIN D1AESION 01(400) INTEGE7 P,0,00, R, RR, N,MM, MN, K PI=3,1415,26636 V=1.6007P1 THIS PROGRAM IS SIMILAR TO "ECHOES" EXCEPT THAT VALUES COPRESPONDING TO B3TH LO AND TO FEROPENCIES ARE TAKEN THE METHOD SHUGYED IS IDENTICAL TO B3TH LO AND TO FEROPENCIES ARE TAKEN THE METHOD SHUGYED IS IDENTICAL TO B3TH LO AND TO FEROPENCIES ARE TAKEN THE METHOD SHUGYED IS IDENTICAL TO B3TH LO AND TO FEROPENCIES ARE TAKEN THE METHOD SHUGYED IS OFFICE B3TAILE PROGRAM IS SIMILAR TO "ECHOES" EXCEPT THAT VALUES COPRESPONDING TO B3TH LO AND TO FEROPENCIES ARE TAKEN THE METHOD SHUGYED IS IDENTICAL B400 SECONDEST IN PITROTPAL ONLY SUBROUTINE "CLASOSC" IS DIFFERENT THIS USES T METHOD OF GERVAIS AND PIRIOU TO CALCULATE VALUES OF "ECHOES" THIS PROGRAM SHOULD ONLY BE USED WHEN WIDE REFLECTANCE BANDS APE D3TAILE" FOR FULLER D3GIPTION OF PARAMETRS AND USE OF SUBROUTINES SEE "ECHOESS" IN PROTON SIN SPECTRUM MENO OF OSCILLATORS=,15) NED OF POINTS IN SPECTRUM MENO OF OSCILLATORS FREQUENCIES REDUIRED TAKEN=,5(2X,F12.6)) WRITE (6,239) 295 FORMAT(12)H MAVELENGTHS TAKEN=,5(2X,F12.6)) WRITE (6,239) 295 FORMAT(12)H MAVELENGTHS TAKEN=,5(2X,F12.6)) WRITE (6,230) (MI(1),71(1),J=1,M) WRITE (6,201)KX READ(S,102)KX READ(S,102)KX MRITE (6,201)KX READ(S,102)KX MRITE (6,201)KX READ(S,102)KX MRITE (6,201)KX READ(S,102)KX MRITE (6,201)KX READ(S,102)KX MRITE (6,301)K MRITE (6,301)K MRITE (6,303)R 300 FORMAT(2)H KEFTECTIVITIES TAKEN=,5(2X,F10.6)) 0 CONTROL NOR SPECTRUM OF LIMIT FREQUENCIES WRITE (6,303)R 303 FORMAT(2)H S,OL.F,F,=,I5) 0000000000 THE C CCC OF TO MODE Z1 DAMP. CONST. OF TO MODE F LO MOD**E**. C Q=1 WRITE(6,303)R 303 FORMAT(11H S.O.L.F.=,I5) WRITE(6,304)Q 304 FORMAT(13H CONTROL NO=,I5) WRITE(6,304)Q 4 FORMAT(13H CONTROL NO=,I5) Q0=0+1 WRITE(6,650)Q0 0 FORMAT(4H Qu=,I5) RR=P=1 WRITE(6,651)RR CALL GRAPHIC(1,A1) D0 501 I=1,N A1(I)=41(I)/100.000 C1(I)=ALOG(SQPT(A1(I))) 1 CONTINUE CALL CURVE 4 FORMAT(2F10.3) 1 FORMAT(2F10.3) 1 FORMAT(2F10.5) 0 FORMAT(2I5) 1 FOEMAT(3H THE OSCILLATOR PARAMETERS ARE,2X, 119H CPSILON INFINITY=,F3.1) 1 FOEMAT(15H THE OSCILLATOR PARAMETERS ARE,2X, 119H CPSILON INFINITY=,F3.1) 1 FOEMAT(15H THE OSCILLATOR PARAMETERS ARE,2X, 119H CPSILON INFINITY=,F3.1) 1 FOEMAT(16H TO FREQUENCY=,F10.6,2X,20H TO DAMP. CONSTANT=,F10.5) 2 FORMAT(14H LO FREQUENCY=,F10.6,2X,20H LO DAMP. CONSTANT=,F10.5) 3 FORMAT(15H TL) FREQUENCY=,F10.6,2X,20H LO DAMP. CONSTANT=,F10.5) 3 FORMAT(14H LO FREQUENCY=,F10.6,2X,20H LO DAMP. CONSTANT=,F10.5) 3 FORMAT(15H TL) FREQUENCY=,F10.6,2X,20H LO DAMP. CONSTANT=,F10.5) 3 FORMAT(14H LO FREQUENCY=,F10.6,2X,20H LO DAMP. CONSTANT=,F10.5) 3 FORMAT(15,6) CALL KKCYOLE(01) CALL CLADIS(01) CALL GRAPHIC(0,D1) STOP END 650 501 $104 \\ 651 \\ 100$ 101
200 201 202 103

```
SUB POUTINE CLASOSC
COMMON A1(+00),B1(400),C1(400),E1(400),F1(400),
1*1(15),Z1(15),W2(15),Z2(15),T(+00),A2(400),C2(400),
2P,Q,QQ,R,R=,N,MM,PI,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN
COMPLEX C,X1,X2,EPSILON
INTEGET P,Q,QQ,R,RR,M,MM,MN,K
DO 10 I=1,N
B=B1(I'*31(I)
C=CMPLX(1.0,0.0)
DO 20 J=1,MM
W0=W1(J)*W1(J)
W1=W2(J)*W2(J)
X=WO-8
Y=Z1(J)*B1(I)
X1=CMPLX(X,Y)
A=WN-8
D=Z2(J)*B1(I)
X1=CMPLX(X,Y)
A=WN-8
D=Z2(J)*B1(I)
X2=CMPLX(A,D)
C=C*X2/X1
D CONTINUE
EPSILON=CMPLX(EPREAL, =EPIMAG)
EPSILON=CMPLX(EPREAL, =EPIMAG)
EPSILON=CMPLX(EPSILON)
E1(I)=EPIMAG
E=SQRT(E1(I)*2+F1(I)*2)
F=SQRT(E1(I)*2+F1(I)*2)
F=SQRT(E1(I)*2+F1(I)*2)
F=SQRT(E1(I)*2+F1(I)*2)
F=SQRT(E1(I)*2+F1(I)*2)
F=SQRT(E1(I)*100.00
CONTINUE
RETURN
END
20
 10
```

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000 C С C С С С С С С FORMAT(7H THETA=,5(2X,F10.6)) CALL GRAPHIC(-1,X1) CALL GRAPHIC(-1,Y1) CALL GRAPHIC(0,G1) CALL GRAPHIC(0,H1) CALL GRAPHIC(0,Q1) RETURN END 905

240.

С	<pre>SUBJOUTINE CEADIS(1)),C1(400),E1(460),F1(460), (COMMON A1(400),B1(400),C2(400),C2(400),C2(400), 2P,Q,QQ,R,RR,N,MM,PI,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN DIMENSION 01(400) INTESER P,0,QQ,R,RR,M,MM,MN,K CALCULATE INTEGRAL FROM KRAMERS KRONIG OUTPUT SPECTRA E=0.000 DO 20 I=QQ,RR P=I+1 IF(P,GT.RR)GO TO 20 A=D1(I)/B1(I) B=D1(P)/B1(P) C=B1(P)-B1(I) D=V*(C*A+C*B) E=E+D T(I)=E 20 CONTINUE WRITE(6,203) (T(I),I=QQ,RR) WRITE(6,203) (T(I),I=QQ,RR) 203 FORMAT(26H THE KK OSC. STRENGTH V1=,5(2X,F10.4)) RETURN END</pre>
0000000	SUBROUTINE GRAPHIC(MN,D1) COMMON A1(400),B1(400),C1(400),E1(400),F1(400), 1W1(15),Z1(15),W2(15),Z2(15),T(400),A2(400),C2(400), 2P,Q,QQ,R,RE,N,MM,PI,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN DINENSION D1(400) INTEGEP P,D,QQ,R,RR,M,MM,MN,K DATA FOR PLOTTER TAKES WAVELENGTHS,AND VARIABLES, FINDS MAX AND MIN AND ADJUSTS VALUES ACCORDINGLY TO GIVE ARBITRARY UNITS WHEN MN=0,-1 WHEN MN=1 NO SCALING VALUES ARE PLOTTED AS CALCULATED K= NUMBER OF SETS OF DATA M= NUMBER OF OUTPUT POINTS FW= FINAL WAVENUMBER WI= INITIAL WAVENUMBER
-	<pre>K=8 M= (22-00)+1 FW=31(23) WI=31(00) WRITE(1,31)FW,WI,M,K WRITE(1,30) (31(1), I=00,R2) IF(MN) 500,404,405 404 YMAX=50.0 YMIN=10.0 D0 400 I=00,R2 IF(91(I).LT.YMIN) G0 TO 401 IF(01(I).GT.YMAX) G0 TO 402 G0 TO 400 401 YMIN=01(I) G0 TO 400 402 YMAX=01(I) 400 CONTINUE G0 TO 1 500 YMAX=4.0 YMIN=0.5 D0 501 I=00,R2 IF (01(I).LT.YMIN) G0 TO 502 IF (01(I).GT.YMAX) G0 TO 503 G0 TD 501 F02 YMAX=01(I)</pre>
	GO TO 501 GO TO 501 503 YMAX=D1(I) 501 CONTINUE 1 DO 403 I=QQ,RR D1(I)=(D1(I)-YMIN)*100.00/(YMAX-YMIN) 403 CONTINUE 405 WRITE(1,30) (D1(I),I=QQ,RR) 30 FORMAT(6F9.3) 31 FORMAT(F5.0,2X,F4.0,2X,I3,2X,I2,60X) RETURN END

22

SUBSOUTINE DURYE COMMON A14000 bit(s00).C1(400).F1(400).F1(400). Dif(s).Z(100).W2(15).W2(15).Z2(10).f(400).A2(400).C2(400). Dif(s).Z(100).W2(15).W2(15).W2(10).C1(400).C2(400).C2(400). Dif(s).S(100).W2(15).W2(10).S(10).S(10).S(10).C2(400).C2(400). Dif(s).S(10).W2(15).W2(10).S(1 SUBROUTINE FUNSET(M4, X, STEP, FVEC) DIMENSION X(M4), STEP(M4), FVEC(M4) CALCULATES FUNCTION VALUES SO THAT D DO 10 I=1,M4 Y=X(I) X(I)=Y+STEP(I) CALL FUNCT(M4,X,Z) FVEC(I)=Z X(I)=Y 10 CONTINUE RETURN END DERIVATIVES MAY BE ESTIMATED С

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Loading of programs

All three programs have data input formats identical. This enables the same punched card deck to be used for any of the three programs. The data is fed into the programs in the following order:

- Total number of data points taken; number of reflectance bands (215 format).
- 2. Frequencies of the data points used (3F10.6 format).
- Oscillator parameters (see section on oscillator parameters).
- Reflectivities (in %) of the data points used (3F10.6 format).
- Highest <u>reliable</u> data point (limit of observed data before extrapolation) (I5 format).
- 6. l (first data point) (I5 format).

For the meaning of output parameters, see Chapter Two, section A.

Oscillator parameters

For a meaning of each parameter and methods of estimating them see Chapter Two, section A.

Appendix 1 does not use oscillator parameters and no estimates are required. For Appendix 2 estimates of the following are required:

- 1. visible light refractive index (ε_{∞}) (F3.1 format).
- Oscillator strength; Transverse optic mode frequency; damping constant (3F10.6 format).

For Appendix 3 estimates of the following are required:

- 1. Visible light refractive index (ε_{∞}).
- Transverse optic mode frequency; damping constant (2F10.3 format).
- Longitudinal optic mode frequency; damping constant (2F10.3 format).