A Synchrotron Radiation Study of the Epitaxial Growth of Rare Earth Metal Overlayers and Their Magnetic Properties

> Thesis submitted for the degree of Doctor of Philosophy at the University of Leicester

> > by

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October 1996

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Abstract

The structural and magnetic properties of rare earth metal overlayers have been investigated using techniques utilising synchrotron radiation.

The magnetic ordering in ultrathin Tb layers was studied using Spin Polarized Photoelectron Diffraction. Magnetic information is obtained from the variation with temperature of the relative intensity of the peaks in the Tb 4s multiplet splitting. Short range magnetic order is shown to exist in the ultrathin Tb film up to temperatures significantly higher than the bulk transition temperature.

The growth mode of Gd films on Mo(110) was investigated using Surface X-ray Diffraction. The formation of the Gd adlayer was found to change with substrate temperature. At room temperature the growth mode was Stranski-Krastanov, but at higher temperatures, the growth proceeds by step-flow and the reflected X-ray intensity decays. The growth curve is parabolic at the start of deposition up to 1monolayer before becoming a constant value for the duration of the deposition.

The epitaxial growth was found to improve if the substrate was first exposed to a controlled dosage of oxygen gas. Oscillations in the reflected X-ray intensity were observed up to a coverage of 7 monolayer. It is proposed that oxide clusters form on the surface and act as nucleation sites which facilitate epitaxial growth.

The magnetic properties of ultrathin Gd films have been studied using Circular Magnetic X-ray Dichroism. To induce magnetisation in the Gd film, a buffer layer of Fe was deposited on to the Mo(110) substrate prior to deposition of the Gd film. Sum rules were used to calculate the expectation value of the orbital angular momentum operator, $\langle L_z \rangle$, which was found to increase as the thickness of the Fe buffer layer was increased.

To Gran

Acknowledgements

I would like to thank my supervisor Professor Colin Norris for his guidance and providing motivation throughout the duration of my doctoral research.

Dr. Chris Binns and Dr. Chris Nicklin deserve extra thanks for providing technical instruction in sample preparation, data collection and analysis, especially in the early part of my work.

I must thank Mr Steve Taylor, Mr Stuart Thornton and the technical staff of the Department of Physics and Astronomy at Leicester University for their advice and assistance, without which my experiments might not have been possible.

Thanks also to the science and technical staff at the Daresbury Synchrotron Radiation Source for their assistance in performing my experiments.

I should mention the rest of CMP, each of whom has been a great source of entertainment. They are; Cath, Paul, Anthony, Steve, Mark, Kevin, Nigel, Martin and Richard. Also, from the theory group; Merv, Frank and Gary.

I would like to thank the EPSRC for awarding me a studentship to carry out this work.

Finally, my parents, Phyllis and Alex, and my brother Simon deserve special thanks for their support and encouragement.

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Chapter 1

Introduction

The physical properties of a crystalline solid are determined by the type and distribution of the atoms within the three dimensional lattice. Any change in the geometric arrangement will affect the physical properties of the material. The surface of a crystal can be pictured as the termination of a semi-infinite lattice. The atoms at the surface have a lower coordination than atoms in the bulk and in consequence the surface can exhibit properties that are significantly different from the bulk phase. A good example is the rearrangement of atoms within the outermost layers parallel and perpendicular to the surface plane, an effect referred to as reconstruction and relaxation.

Since all properties are in some way related to the atomic geometry, it follows that a change in one will affect the other. Thus magnetic and electrical properties can be dramatically altered at a crystal's surface. Enhanced magnetic moments are known to exist for some elements of the first row of the transition metals; those with a partially occupied 3d shell [1, 2]. Magnetism has even been reported for 4d elements which are normally paramagnetic [3].

A particularly interesting group of magnetic metals is the rare earths (lanthanides) extending from cerium to ytterbium in the periodic table. The unique behaviour of the rare earths is associated with the partially filled and highly localised 4f states. Although only weakly bound they show, with the exception of cerium, only little intermixing with the extended 5d6sp valence states. They are more appropriately described within a many-body approximation rather than the more usual one-electron model. Rare earth metals and alloys present a valuable opportunity for studying the effects of strong atomic-like correlations perturbed by the presence of a non-localised conduction band. These include intermediate or mixed valence [4, 5] and heavy fermion behaviour [6, 7].

In recent years much of the attention has concerned the modifications that take place at surfaces and interfaces [8, 9] in part because of the potential application to technology. Rare earths alloyed with transition metals are known to exhibit exceptionally high catalytic activities for some commercially important reactions [10, 11] and rare earth-semiconductor interfaces have shown unusually low Schottky barrier heights [12]. The high reactivity and the difficulty in preparing high purity bulk single crystal rare earths has, however, inevitably delayed progress in this field.

With methods such as molecular beam epitaxy (MBE) it is now possible to produce metal structures of unprecedented perfection and novel design. The technique has been widely used for the production of semiconductor heterostructures and now increasingly for growing artificial structures of metals. Effects such as giant magnetoresistance which have been observed with metal multilayers [13-15] confirm the potential technological significance of such structures and the importance of ultrathin metallic layers. The details of the atomic mechanisms involved in MBE and how they are related to the presence of impurities, steps and other surface details are still not well understood. A precise knowledge of the atomic structure at metal surfaces and in ultrathin films will lead to a better control of the complex processes involved in their growth and to the development of new and improved magnetic devices.

Techniques such as low energy electron diffraction (LEED) [16] and Auger electron spectroscopy (AES) [17, 18] have been routinely used to determine atomic structure and composition at surfaces for many years. They rely on the strong coulombic interaction of low energy electrons with atoms to achieve surface sensitivity. More recently, scanning probe microscopy [19-21] has been used to image the top layer of the surface with atomic resolution. With the introduction of intense synchrotron radiation sources, other techniques have become available which utilise the interaction of electromagnetic radiation with matter and these have greatly assisted the study of surfaces. Surface X-ray diffraction (SXRD) has become well established over the last decade as a powerful probe of surfaces and interfaces [22, 23]. The power of the technique derives from the weak scattering of X-rays by matter. This allows a simple analysis of the scattered intensities based on the single scattering or kinematical approximation which gives a direct insight into the atomic geometry.

Photoelectron spectroscopy (PES) is a simple process yet a very powerful tool for the study of surfaces. Incident photons on the sample provide electrons with sufficient energy to reach a higher state and escape the solid. The direction and kinetic energy of these photoelectrons provide information on the distribution of the initial states. Magnetic information can also be obtained from the relative intensity ratio of core s level multiplet splittings in magnetic materials and this property is exploited in spin polarized photoelectron diffraction (SPPED) experiments [24-26].

Dichroism is a general term which encompasses photoemission and absorption measurements and utilises the fact that only certain electronic transitions are allowed when the incident radiation is of a particular polarity. Circular magnetic X-ray dichroism (CMXD) derives magnetic information from absorption spectra [27, 28] where the incident radiation is circularly polarized. Conservation of angular momentum decrees which electronic transitions are allowed and these are manifested by changes in the lineshapes of the absorption spectra when the helicity of the incident radiation is reversed. The normalised, background-subtracted, intensities of the peaks can be used in conjunction with derived sum rules [29, 30] to evaluate expectation values for quantum mechanical operators.

In this thesis a study is reported of the magnetic properties of rare earth metals and the growth of an epitaxial rare earth film studied using synchrotron radiation. Chapter 2 gives a background to the rare earth metals and their properties. In chapter 3 an explanation of the experimental apparatus is given with descriptions of the facilities used at the Daresbury Synchrotron Radiation Source (SRS). The experimental techniques and a brief treatment of the theory involved are presented in chapter 4. The techniques described are those used in the work presented here and a brief outline is also provided at the beginning of each relevant chapter.

Terbium is of interest as a magnetic rare earth and has been studied using Spin Polarized Photoelectron Diffraction (SPPED) and the results are presented in chapter 5. This technique is ideally suited to short range magnetic order because it samples diffraction effects of the photoelectron which are influenced only by the nearest neighbour interactions. The hole resulting from PES will thus be aligned either parallel or antiparallel to the unpaired electrons in the ion's 4f shell and this will alter slightly the binding energy of the 4s level. This effect is called multiplet splitting and is simplest to understand in the case of core s levels where the splitting is simply a doublet. Photoelectrons are scattered differentially depending on whether their spin is aligned parallel or antiparallel to the unpaired spins of the 4f electrons in the ions surrounding the emitting ion. The variation with temperature of the intensity ratio of the doublet peaks in the photoemission spectrum thus provides the information as to the temperature at which short range magnetic order is lost. It is shown that short range magnetic order persists to temperatures above twice the Néel Temperature of Tb, and the order does not appear to be confined to atoms in a particular environment such as those at the surface or interface, but the magnetic order persists in 'pockets' throughout the whole film.

In chapter 6, SXRD has been used to determine the growth mode of Gd deposited on Mo(110). The intensity of the reflected X-ray intensity is recorded as a function of deposition time and the variation of the intensity provides information on the growth mode of the adlayer. It is shown that the growth mode changes as a result of raising the substrate temperature and also by dosing the substrate with high purity oxygen gas which improves the epitaxial growth of the adlayer. At room temperature the growth mode agrees with previous studies [31] which suggests that a flat monolayer forms before the growth becomes progressively rougher. The third layer begins before the completion of the second. The adlayer islands coalesce as the overlayer thickens. When the substrate temperature is increased the islands form immediately on completion of the first monolayer; Stranski-Krastanov growth. The growth mode of Gd changes dramatically when the Mo(110) substrate is pre-dosed with oxygen. Layer-by-layer growth was observed to persist for up to 7 monolayers indicated by oscillations in the reflected X-ray intensity. It is proposed that gadolinium oxide clusters form at the substrate surface and the interlayer transport is enhanced in subsequent layers precluding the formation of islands.

Gd is one of the most studied of the magnetic rare earth elements by virtue of its half-filled 4f shell. All the 4f electrons have the same spin and the values of most of the magnetic parameters are a maximum for Gd. The magnetic properties of ultrathin Gd films have been studied using circular magnetic X-ray dichroism (CMXD) and this reported in chapter 8. This technique is only possible with synchrotron radiation because the radiation

needs to both circularly polarized and tuneable to the energies required for absorption, which vary from element to element. In chapter 7 is shown the results of a CMXD study in the 3d4f absorption of ultrathin Gd films deposited on a Mo(110) substrate. It will be shown that while no dichroism is observed at room temperature for Gd films deposited directly on the Mo(110) substrate, dichroism was observed when an Fe film was deposited on the Mo(110) substrate prior to deposition of the Gd adlayer. Dichroism is simply the difference in the absorption signal of a magnetised sample when the helicity of the incident polarized radiation is reversed. The difference in the absorption intensities is used with sum rules to provide expectation values for the orbital angular momentum operator $\langle L_Z \rangle$.

4

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Chapter 2

The Rare Earths

- 2.1 General Properties and Applications
- 2.2 Structural Properties

Bulk

Surface

Rare Earth Overlayers

2.3 Electronic Structure

Core Level Spectroscopy

X-ray Photoemission Spectroscopy

X-ray Absorption and Emission Spectra

Choice of Core Hole

 $d \rightarrow f$ Transitions (M_{4,5}, N_{4,5})

2.4 The Relation Between Electronic Structure and Magnetic Properties of the

Lanthanide Metals

Indirect Exchange Interaction

The Relation Between Band Structure and Magnetic Ordering

Conduction Electron Polarization

2.5 Magnetism in Rare Earths

Neutron Diffraction Investigations of Magnetic Structures

Magnetization and Susceptibility

Magnetic Anisotropy

References

2.1 General Properties and Applications

The rare earth elements extend from La to Lu in the Periodic Table. They are also commonly referred to as lanthanides after the first element in the group. The very similar chemical and physical properties of the lanthanides makes for great difficulty in separating them from the naturally occurring ores.

Though the rare earths have very similar chemical properties their electronic, structural and magnetic properties can vary greatly and it is the differences in these properties that have been the subject of much research over many years. The electronic and structural properties of the rare earths are summarised in Table 2-1 [1].

The rare earth metals have several applications which are of interest to materials scientists. They include;

(i) catalysts

(ii) constituents of materials used for permanent magnets, such as $SmCo_5$, Sm_2Co_{17} , NdFeB (iii) as a constituent of high temperature superconductors.

The high reactivity of the rare earths is an obstacle to studying the electronic, structural and magnetic properties of the pure metals. These properties can be significantly altered if the metals are contaminated. Thus, once purified it is important to limit the exposure to gases such as oxygen and hydrogen and they are usually stored in an inert argon atmosphere. To study surfaces of rare earth metals with minimum contamination it is necessary to prepare pure samples under UHV conditions, for example by vapour deposition from a well outgassed vapour source as described in §3.4.2.

2.2 Structural Properties

Bulk

Rare earth metals exist naturally in one of five crystal structures. Eu is body-centred cubic (bcc), Sm is rhombic, and the rest adopt one of the close packed structures – hexagonal close packing (hcp), double hexagonal close packing (dhcp) or face-centred cubic (fcc). If the three inequivalent sites of a two-dimensional hexagonal lattice are labelled as A, B, C then the crystal structures can be defined in terms of layers of these 2 dimensional hexagonal lattices, for example hcp can be expressed as ABAB, dhcp as ABAC, fcc as ABC and rhombic as ABABCBACA. These 3 dimensional lattice structures are shown in figure 2-1. Ideal close packing would result in an ideal lattice parameter ratio $\frac{9}{a} = \sqrt{\frac{9}{3}} = 1.633$. The structures listed in Table 2-1 are those adopted by the elements at room temperature. However, most of the elements change their crystal structure on the external application of temperature or high pressure. The sensitivity of the crystal structures to temperature and

Element	Symbol	Z	A	Electronic	Radius	(A)	Crystal	Lattice	Parameters	
				Configuration		- 11 - T - T - T - T - T - T - T - T - T	č	,		
				(solid state)	lonic	Metallic	Structure	a	ა	2 a
Scandium	Sc	21	45	(3d4s)3	0.785	1.641	hcp	3.309	5.268	1.592
Yttrium	Y	39	89	(4d5s) ³	0.880	1.801	hcp	3-648	5.732	1.571
Lanthanum	La	57	139	4f ⁰ (5d6s) ³	1.061	1.879	dhcp	3.774	12.171	1.612†
Cerium	ථ	58	140	4f ¹ (5d6s) ³	1.034	1.825	fcc	5.161	1	1
Praesodymium	Pr	59	141	4f ² (5d6s) ³	1.013	1.828	dhcp	3.672	11.833	1.611†
Neodymium	PN	60	144	4f ³ (5d6s) ³	0.995	1.821	dhcp	3.658	11.797	1.612†
Promethium	Pm	61	145	4f ⁴ (5d6s) ³	0-979	1.811	dhcp	3.650	11.650	1.595†
Samarium	Sm	62	150	4f ⁵ (5d6s) ³	0.964	1.804	rhombic	3.629	26.207	1.605†
Europium	Eu	63	152	4f ⁷ (5d6s) ²	0.950	2.042	bcc	4.583	1	1
Gadolinium	Gd	64	157	4f ⁷ (5d6s) ³	0.938	1.801	hcp	3.634	5.781	1.591
Terbium	đT	65	159	4f ⁸ (5d6s) ³	0.923	1.783	hcp	3.606	5.697	1.580
Dysprosium	Dy	99	163	4f ⁹ (5d6s) ³	0.908	1.774	hcp	3.592	5.650	1.573
Holmium	Ho	67	165	4f ¹⁰ (5d6s) ³	0.894	1.766	hcp	3.578	5.618	1.570
Erbium	Er	68	167	4f ¹¹ (5d6s) ³	0.881	1.757	hcp	3.559	5.585	1.569
Thulium	Tm	69	169	4f ¹² (5d6s) ³	0-869	1.746	hcp	3.538	5.554	1.570
Ytterbium	Yb	70	173	4f ¹⁴ (5d6s) ²	0.858	1.939	fcc	5.485	1	
Lutetium	Lu	71	175	4f ¹⁴ (5d6s) ³	0-848	1.753	hcp	3.505	5.549	1.583

[†] For the dhcp and rhombic crystal structures, $\frac{c}{2a}$ and $\frac{2c}{9a}$ have more relevance.

Table 2-1. Physical properties of the rare earth elements.

Spheres arranged in a close-packed layer.







Bottom layer A Middle layer B Top layer C

The top layer C can sit in one of two orientations.



hcp







Figure 2-1. The manner in which close-packed layers can be stacked in sequence produces the hcp, dhcp, fcc and rhombic structures found in the rare earth elements.

pressure imply that the energy difference between different crystal structures is relatively low and, therefore, it is reasonable to suppose that surface structures will be different to that of the bulk.

By convention, the RE metals are subdivided into two groups – the 'light' and 'heavy' rare earths. The light rare earths are those elements La to Sm while the heavy rare earths are Gd to Lu. Within each group the chemical properties of the elements are very similar and consequently are commonly found together in natural mineral deposits. All the heavy rare earths adopt the hcp crystal structure while the light rare earths (with the exception of Sm) are dhcp.

Surface

Surface studies have concentrated on the hcp (0001) face since it is the most easily prepared orientation and has been modelled in band structure calculations. Low Energy Electron Diffraction (LEED) measurements on various systems have shown that there is relaxation at the surface with respect to the bulk structure. For example, the Tb(1120) surface shows contraction by 3.3% of the first interlayer spacing and a parallel translation of the surface atoms by 0.21Å with respect to the bulk [1]. Gd(1120)also shows a reconstruction similar to Tb with a first interlayer contraction of 2.7% and a second interlayer contraction of 1% [1].

Rare Earth Metal Overlayers

Many systems have been studied by growing epitaxial layers onto various substrates. The ideal substrate on which to study adatom-adatom interaction is one that ensures thermodynamic stability of a two dimensional layer at submonolayer coverages and there is no reaction between adlayer and substrate. For this reason the densely packed (110) surfaces of refractory metals such as W and Mo are frequently chosen as substrates. Generally at submonolayer coverages the overlayer forms one or more $(n \times 2)$ structures $(3 \le n \le 10)$ which indicates constant ordering in the $[1\overline{10}]$ direction with a gradual contraction in the [001] [1, 2]. At monolayer coverages hexagonal or pseudo-hexagonal overlayers are observed and further deposition tends to be layer-by-layer with the overlayer gradually translating into the bulk crystal structure.

Each of the rare earth metals exists in one of five crystal structures as listed in Table 2-1 [1]. At room temperature nine exist in the hcp structure, four in a double c-axis hcp structure (called dhcp), two are fcc and one each are bcc and rhombic. With the exception of the Eu bcc structure, all the other crystal structures are close-packed with each atom having 12 nearest neighbours, the maximum coordination number. From Table 2-1 it can be seen that the lattice parameter ratio $\frac{9}{4}$ for the hcp RE metals fall in the range 1.57 to 1.59, approximately 3% less than the ideal value of 1.633. This indicates that the atoms in the

basal (hexagonal) plane are dilated by $\sim 3\%$ with respect to close packing. The corresponding values for the dhcp and rhombic structures indicate a similar expansion (when taking into account the extra atoms in the unit cell).

It is of interest to note that when considering the close packed crystal structures only, that there is a systematic variation of the room temperature structures along the series as the hcp structure gradually takes over from the fcc.

Element	La-Ce		La–Pm		Sm		Gd-Lu
fcc:hcp	1:0	⇒	$\frac{1}{2}:\frac{1}{2}$	⇒	$\frac{1}{3}:\frac{2}{3}$	⇒	0:1
crystal structure	fcc		dhcp		rhombic		hcp

The rhombic crystal structure of Sm can be regarded as a mixture of one part fcc and two parts hcp. The dhcp structure can be viewed as an equal mix of fcc and hcp. La and Ce have been included in both fcc and dhcp categories as they have a dhcp \rightarrow fcc transition close to room temperature.

The application of high pressure causes the elements to revert to the previous structure in the series [1], that is Gd and Tb become rhombic, Sm becomes dhcp, La, Pr and Nd become fcc. Skriver [3] suggested that the sequence of crystal structures could be explained by the variation in the occupancy of the d-band across the series. His band structure calculations showed a systematic decrease in the d-band occupancy for the trivalent lanthanides.

2.3 Electronic Structure

The electronic configuration of the rare earths is of the form $[Xe]4f^{n}(5d6s)^{v}$ where n is the occupancy of the 4f level and v is the occupancy of the valence band. The rare earth metals are characterised by a gradual filling of the 4f level across the series. The partially filled 4f levels are highly localised within the atom and, although weakly bound, there is very little overlap with the 5d6s valence band. This is illustrated in figure 2-2 which shows the radial distribution function of the energy levels calculated from Hartree-Fock theory [4]. The degree of overlap varies across the series as shown in figure 2-3 [5], which indicates the expectation values for the radii of the various orbitals as a function of atomic number. There is a sudden drop of the 4f orbital value at the start of the lanthanide series followed by a slow decrease across the group caused by incomplete screening of the 4f electrons as the nuclear charge increases. Accompanying this is a slower decrease of the 5d and 6s radial distribution values resulting in a reduction of the overlap between the 4f level and the valence band. This is the phenomena known as 'lanthanide contraction'.

For almost all the rare earths there is change of valency on condensation from the atomic state to the solid state. Generally, the free atoms are divalent while in the metallic state



Figure 2-2. The radial charge density $R_{n\ell}^2(\mathbf{r})$ as a function of r for the 4f, 5s, 5p, 5d, 6s and 6p electrons of CeI.



Figure 2-3. The computed expectation values of r for various orbitals in the excited $4f^{n-3}5d6s6p$ configurations of neutral lanthanides. (For LaI, the 4f6s6p and 5d6s6p configurations were considered).

they are trivalent, but there are exceptions as shown in Table 2-1. The change in valency is driven by the increase in cohesive energy in the solid state which provides the extra energy required to promote a 4f electron into the (5d6s) valence band. Some rare earths have an energy difference between the divalent and trivalent states that is so small that in sites of low coordination the atom can have a different valency to that of a higher coordinated atom. For example, Sm has divalent surface atoms while the bulk atoms are trivalent [6]. The energy difference can be estimated by considering the energy diagram shown in figure 2-4 [6]. The cohesive energies, E_{coh} , for divalent and trivalent metals are well known and the energy, U_m^S , required to form a mole of surface atoms has been shown empirically [7] to be,

$$U_m^s \sim 0.2 E_{coh}$$

Johansson calculated the energy differences between di- and tri-valent states across the series and the results are shown in figure 2-5 [6]. The lines labelled 'surface', 'edge' and 'corner' give a general idea of the energy gain for atoms in these sites. These results show that Eu and Yb should be divalent in all states and Sm to be divalent at the surface on a trivalent bulk. For some metals, for example Tm, valence instability should be expected in atoms with lower coordination such as those at edge and corner sites leading to a mixture of valences on the surface, subsequently observed by Alleno [8].

Core Level Spectroscopy

Strictly speaking, the 4f levels of the lanthanides are neither wholly valence band nor wholly core level. They are partially occupied and degenerate with the valence band, which indicates that perhaps they should be considered as valence electrons. However, due to their localised character and subsequently negligible role in bonding, they are usually treated as core levels in electronic structure calculations. In contrast, the p levels at binding energies of $\geq 20eV$ are fully occupied in all the rare earths and have always been treated as core levels. (N.B. Calculations by Temmermann and Stone [9] show that the p levels of rare earths have a significant effect on the determination of the lattice constant, indicating that they are not true core levels, and they coined the term "semi-core levels").

X-ray Photoemission Spectroscopy

For X-ray photons in the energy range of approximately 1keV, the final energy of the photoelectron is so high that its wave function is very nearly a plane wave. Since a plane wave contains a large number of angular momentum states, the probability of exciting an electron out of the 4f shell becomes favourable. This is therefore a powerful tool to probe the structure of the partially filled 4f shell of the rare earth metals.



Figure 2-4. Energy diagram for Sm showing the cohesive energies for the divalent and trivalent metals. Also shown are the energy differences between surface and bulk atoms.



Figure 2-5. Diagram showing how atomic valency changes with coordination for all the elements in the rare earth series.

Electrons in the 4f shell move in a highly correlated manner, so the excitation process cannot be visualised in a quasi-particle picture. The energy required to promote one electron from a 4f shell to a 5d state at the Fermi level, $E(4f^{n-1}5d) - E(4f^n)$, is called the electron promotion energy and represents the measured 'position' of the 4f level.

The XPS spectrum of 4f excitation is characteristically a series of peaks corresponding to the multiplet structure of the final 4f shell. The splitting of the final states with different L quantum numbers in the Russell-Saunders scheme is evident in Sm and the heavier elements. The spin-multiplet structure is seen in rare earths with more than a half-filled 4f shell (Tb-Tm). For example, the final state of Tb (4f⁷) may be $4f_{\uparrow}^7$ (S = $\frac{7}{2}$) or $4f_{\uparrow}^64f_{\downarrow}^1$ (S = $\frac{5}{2}$). The splitting of these groups of states measures the exchange interaction between the 4f electrons.

The XPS method also measures, with high resolution, the structure of the valence bands of transition and rare earth metals. The formula of the optical density of states (ODS) is the same as for Ultra-violet Photoemission Spectroscopy (UPS),

$$D(E,\omega) = \frac{2\pi e^2}{m^2 c^2 \hbar \omega} \sum_{i,f} \sum_{k} \left| M_{if} \right|^2 \delta \left[E - E_f(\mathbb{k}) \right] \cdot \delta \left[E - \hbar \omega - E_i(\mathbb{k}) \right]$$

For constant matrix elements, $D(E, \omega)$ is proportional to the product of the initial and final densities of states.

$$D(E, \omega) \propto N_i(E - \hbar \omega). N_f(E)$$

The final band may be broad because it approaches the free electron band at sufficiently high energy. So $N_f(E)$ is a smooth function and,

 $D(E, \omega) \propto N_i(E - \hbar \omega)$

The XPS spectrum of Gd is shown in figure 2-6 [10]. The single peak from the final state ^{7}F is 8.0eV below the Fermi level. This shows that (like Eu) Gd has an isoelectronic shell; that is, each 4f electron has the same spin. The 4f shell of Gd is far more stable than that of Eu because the Eu single peak is only 2.1eV below the Fermi level.

The XPS spectrum of Tb is shown in figure 2-7 [11]. Tb shows the first instance of exchange splitting where the 7 electrons in the final state may align their spins to get either $S = \frac{7}{2}$ or $S = \frac{5}{2}$. The ⁸S line is 2.3eV below the Fermi level. The next peak is the unresolved line of ${}^{6}P$, ${}^{6}I$ and ${}^{6}D$ and lies a further 5.1eV below the ⁸S line. Similarly, the line for ${}^{6}G$ is expected at 6.2eV, but is observed at 7.0eV and ${}^{6}H$ is expected at 7.3eV, but observed at 8.1eV. This systematic shift of energy levels to higher binding energies reflects the various relaxation processes that take place in the excited atom. The excited 4f shell of Tb sees one more nuclear charge than the ground state 4f shell of Gd and taking the 4f levels as



Figure 2-6. The XPS spectrum of Gd. The peak marked VB is due to the valence band.



Figure 2-7. The XPS spectra of Tb, Dy and Ho.

hydrogen-like orbitals outside the neon core, the effective charges for Tb and Gd are 11 and 10 respectively. Consequently, all the energy level separations of Tb must be scaled up from the corresponding values of Gd by the ratio of the squares of the charges (= $(\frac{11}{10})^2 = 1.21$) [12].

X-ray Absorption versus Photoemission [13]

Through the use of synchrotron radiation sources, high-resolution spectrometers and modern detection techniques, high quality absorption data from all core levels are measurable and can be compared with the corresponding XPS data. The goal of both XAS and XPS spectroscopy is to obtain information about the ground state of the sample under investigation.

The spectra from X-ray absorption experiments are less complicated than those taken in XPS measurements. This distinction between XAS and XPS can be explained by the dipole selection rules where only a small set of states from all the spectral distribution is excited upon creation of the core hole. XPS probes a much larger collection of such final-state multiplets which appear in relatively broad spectra. The relative intensities in the final state multiplets of XAS spectra are well-defined through the dipole selection rules. Therefore XAS spectra exhibit a clearer picture of the atom in the ground state.

The transition in deep core level XAS in the lanthanides can be understood in a oneelectron picture. Satellite structures due to many-electron and final-state effects are found to be insignificant. By contrast, XPS spectra exhibit considerable shake-up intensities, whose interpretation usually needs a set of parameters not determined directly through the experiment at hand nor by other experiments. The much simpler final-state configurations in $M_{4,5}$ absorption have been experimentally demonstrated with 3d-XPS in intermetallic Ce compounds [14]. The $M_{4,5}$ absorption spectra of Ce in α -type mixed valence CeNi₂, CeNi₅ and CePd₃ exhibit only two final-state multiplets, that is $3d^94f^2$ and $3d^94f^1$. On the other hand, the 3d-XPS spectra exhibit the three final-state multiplets, $3d^94f^2$, $3d^94f^1$ and $3d^94f^0$. The reason for the difference seems to lie in the different screening processes involved in XAS and XPS. During $M_{4,5}$ absorption the core hole is completely screened by the 3d photoelectron while during 3d-XPS the screening of the core hole is a much more complicated process. Detailed understanding of the dynamics of screening in XPS is a prerequisite of the correct final-state assignment.

X-ray absorption experiments (in transmission geometry) unambiguously probe the bulk properties of the sample, while XPS is a technique that is sensitive to both bulk and surface. It is difficult to discriminate quantitatively between photoemission from the surface and from the bulk, where the local sites are generally quite different. Very importantly, absorption data of high quality can be routinely obtained from dilute lanthanides (~0.1 atomic per cent) in compounds or alloys using electron or fluorescent yield detection techniques. XPS is restricted to the investigation of more concentrated systems.

Choice of Core Hole.

The two incompletely filled shells of the lanthanides, namely the 4f shell (core electron orbital) and the 5d shell (valence electron orbital) are of particular interest in solid state physics. Many of the challenging anomalies of the lanthanides (for example mixed valence) are connected with the hybridization of the 4f and 5d states. Absorption spectroscopies involving d and p orbitals are experimental methods which examine the unoccupied 4f and 5d states according to the dipole selection rule, $\Delta \ell = \pm 1$. The unoccupied states in the lanthanides can be reached by transitions from deep or shallow core levels. By convention, deep core levels are states in completely filled main shells, that is the K, L and M shells in the lanthanides. Levels in the incompletely filled N and O shells are referred to as shallow core levels, with the exception of 5d which is, of course, a valence electron level. The designation of this classification is made clear by inspection of the different types of absorption spectra observed upon excitation of M and N core levels as shown in figure 2-8 [13]. The d electrons from the shallow N_{4,5} levels (4d \rightarrow nf, n≥4) reach 4f states as do photoelectrons from deep core $M_{4,5}$ level (3d \rightarrow nf, n≥4), but the spectra are completely different [13]. Each of the M_{4,5} spectra exhibits a set of discrete narrow lines. However, the N_{4.5} spectra are dominated by a broad giant resonance above the threshold and exhibits only a weak and extended discrete line spectrum at threshold.

In deep core level XAS the overlap of the core level wavefunction with the wavefunction of the excited state is of little or no importance. Deep core levels may be regarded as classical charge distributions completely screened by the inner shells and the photoelectron. Most of the deep core level spectra can therefore be described without regard to many-electron processes. The large spatial overlap of the shallow 4d wavefunction with the 4f wavefunctions, however, favours relaxation processes of the excited atom involving many-electron effects such as giant resonances.

Spectra with minimised lifetime broadening and final states (largely unaffected by the complicated many-electron effects) occur in $L_{2,3}$ (2p \rightarrow 4f5d) and $M_{4,5}$ (3d \rightarrow 4f) absorption.

$d \rightarrow f$ Transitions (M_{4,5}, N_{4,5})

The required energies for $M_{4,5}$ and $N_{4,5}$ transitions are located in the soft X-ray range (~800-1700eV) and the ultraviolet (~100-200eV) respectively.



Figure 2-8. Absorption spectra with d-f symmetry $M_{IV,V}$ and $N_{IV,V}$ in elemental Ce [8]. The shallow core level $N_{IV,V}$ spectrum exhibits the characteristic 'giant resonance' above the threshold and $4d^94f^2$ multiplet at threshold. The $N_{IV,V}$ multiplet splitting is dwarfed by the large 4d-4f exchange splitting.

M_{4,5} Absorption

When compared with the $L_{2,3}$ spectra, the multiplet splitting of the $3d_{3/2}$ and $3d_{5/2}$ core levels is much smaller (only about 15-45eV) but much larger than the width of the final state multiplets (~10eV). The $M_{4,5}$ spectra exhibit rather sharp $3d^94f^{n+1}$ multiplet structures consisting of several resolvable lines. Each line of this final-state multiplet serves as an indication of the ground state via the number, intensity and position of the line.

The very intense $M_{4,5}$ absorption lines arise from a more or less constant background and are not distorted by a strong absorption edge as are the L absorption lines. Due to the high cross-section of the $3d^{10}4f^n \rightarrow 3d^94f^{n+1}$ transitions, the continuum absorption is nearly indistinguishable from the background.

The M_{4,5} absorption in the lanthanide elements has been investigated systematically by Thole *et al* [15]. They presented calculations of the total $3d^{9}4f^{n+1}$ final state multiplets together with the Δj dipole rule filtered multiplets of all lanthanides. Adjusting the 3d spinorbit splitting and taking into account the 3d lifetime broadening, Thole found good agreement with experimental measurements from rare earth oxides, though Sm was an exception.

2.4 The Relation between electronic structure and magnetic properties of the lanthanide metals. [12]

According to Russell-Saunders coupling scheme, an unfilled atomic shell carries total angular momentum J, and magnetic moment $g\mu_B J$ where J = L + S or |L - S| depending on whether the shell is more or less than half-filled. μ_B is the Bohr magneton and g is the Landé g factor given by,

$$g = 1 + \frac{J(J+I) - L(L+I) + S(S+I)}{2J(J+I)}$$

The Landé g factor is also referred to as the gyromagnetic ratio. For the lanthanide metals with partially filled 4f shells, this moment is possessed by the 4f shell of each atom.

Due to the screening of the 4f orbitals from the environment by the valence electrons, this magnetic moment is not significantly modified in the bulk. This is not the case for the 3d transition metals where orbital angular momentum quenching occurs. In order to produce magnetic ordering in the sample there must be interaction between atoms on different crystal sites. The 4f levels are confined within the atom so any interaction is not due to direct overlap of the 4f orbitals. The communication between sites is, in fact, by an indirect exchange interaction via the conduction electrons – the RKKY interaction. This RKKY interaction is oscillatory as a function of such parameters as electron density and ion separation and is responsible for the rich variety of magnetic phenomena in the rare earths.

At high temperatures, the metals have a Curie-Weiss paramagnetic susceptibility with Curie constants close to $(g\mu_B)^2 J(J+I)$, while at low temperatures the metals become magnetically ordered. For those metals with a ferromagnetic ground state, the saturation magnetization is very close to $g\mu_B J$ per atom.

The following text deals with the question of how magnetic moments on different crystal sites communicate with each other and establish magnetic order. The theory of indirect exchange interaction through the conduction electrons is shown which is then related to the band structure.

Indirect Exchange Interaction

Figure 2-9 shows the radial charge distribution of the 4f, 5d and 6s electrons in the Wigner-Seitz sphere of Gd [16]. The 4f charge distribution drops off rapidly and becomes vanishingly small at the Wigner-Seitz sphere radius. Therefore, it is puzzling as to how the 4f electrons on different atomic sites could interact when there appears to be no overlap between the wave functions. This leads to the s-d model for magnetic transition metals and their alloys which states that the magnetic moments are mainly carried by localised d electrons and, due to the exchange interaction between the d electrons and the conduction electrons (s electrons), a spin density cloud is set up around each atomic site. The direction of the d spin at each site is determined by the net polarization of the s electrons at that site induced by all other spins within a radius measured by the size of the spin cloud. The theory for this type of indirect interaction between nuclear spins in metals and was subsequently called the Rudermann-Kittel-Kasuya-Yosida (RKKY) interaction. Degennes [18] extended the formulation of the RKKY interaction to its application to the lanthanide metals.

There are two main interactions between the conduction electrons and the localised d or f electrons. One is exchange and the other is admixing. The d-f exchange interaction is a straightforward Heisenberg exchange interaction between a conduction electron and an electron in the 4f shell. For simplicity, only one 4f electron with a wave function $\phi_m(r)$ in the angular momentum state (3,m) is assumed. If a conduction electron in band n and wave vector k is scattered by the 4f electron into band n' and wave vector k', the spin-dependent part of the matrix element has the form,

$$M(n\mathbf{k}, n' \mathbf{k}') = -2I_m(n\mathbf{k}, n' \mathbf{k}')s.s_f$$

where
$$I_m(n\mathbf{k}, n'\mathbf{k'}) = \int d^3r_1 \int d^3r_2 \phi_m^*(\mathbf{r}_1) \psi_{n'\mathbf{k'}}^*(\mathbf{r}_2) \cdot \frac{e^2}{\mathbf{r}_{12}} \phi_m(\mathbf{r}_2) \psi_{n\mathbf{k}}(\mathbf{r}_1)$$

 $s \equiv$ spin operator of the conduction electron, and $s_f \equiv$ spin operator of the 4f electron.



Figure 2-9. The radial charge densities of 4f, 5d and 6s electrons in the Wigner-Seitz sphere of Gd metal.

This interaction is basically ferromagnetic, that is there is a tendency for the spin of the conduction electron to line up with the spin of the 4f electron.

Over large distances, the interaction has the spatial dependence $\cos(2k_F R) / R^3$ [12]. The outstanding feature of the coupling energy as a function of distance is the long range oscillatory behaviour which makes it difficult to predict the most stable configuration when the spins become ordered. The wavelength of the oscillation, $\frac{2\pi}{2k_f}$, has the same

origin as the Friedel oscillation which enters many problems involving conduction electrons.

An immediate consequence of the indirect exchange model is the scaling of the paramagnetic Curie temperature of the heavy lanthanides with the Landé factor $(g-I)^2 J(J+I)$. Degennes [18] showed this by using the form of the interaction as given by,

$$J(\mathbf{R}) = \frac{m|\mathbf{I}|^2}{4\pi^3 \mathbf{R}^4} \left[2k_f R\cos(2k_f R) - \sin(2k_f R) \right]$$

Actually, the scaling relation can be proved in a more general way. The high temperature paramagnetic susceptibility of a spin system with its interaction Hamiltonian $H_s = \sum_{i=1}^{n} J(\mathbf{R}_{ij})(g-1)^2 \mathbf{J}_i \cdot \mathbf{J}_j$ is,

$$\chi_p = \frac{N(g\mu_B)^2 J(J+1)}{3k_B(T-\theta_p)}$$

where k_B is the Boltzmann constant and θ_p is the paramagnetic Curie temperature defined by,

$$k_B \theta_p = \tfrac{2}{3} (g-l)^2 J (J+l) \sum_j J(\mathbf{R}_{ij})$$

The heavy lanthanide metals from Gd to Tm are all trivalent in the bulk and have the common hcp crystal structure. It is reasonable to expect that the sum expression in the above equation is nearly the same for all metals in this group. Then it is found that,

$$\theta_p \propto (g-l)^2 J(J+l)$$

and the constant of proportionality can be found by fitting the experimental value for Gd. For the other metals, the values of θ_p predicted from the scaling relation are compared with the experimental values in Table 2-2 [12].
	Gd	Tb	Dy	Ho	Er	Tm
θ_p (theory) (K)	317	211	147	90	51	23
θ_p (experiment) (K)	292.5	217	145	81	47	17

Table 2-2. Comparison of the experimental paramagnetic Curie temperatures for the heavy lanthanides with the scaled theoretical values.

The small discrepancies between theory and experiment are taken as evidence that the electronic structures of these metals are not identical, which was assumed in the calculations for the theoretical values.

Relation between band structure and magnetic ordering.

The types of magnetic ordering are shown in figure 2-10 [19]. The diagram indicates how the total moment in each layer is aligned relative to the atomic plane and how it changes in neighbouring layers. For example, Gd has an in-plane ferromagnetic structure below 293K, while Tb orders first in a helical structure (at 230K) before making a phase transition to the ferromagnetic at lower temperatures (220K).

Consider the helical ordering and let the z-axis be the c-axis of the crystal. Then, the average components of the spins are given by,

$$J_{ix} = A\cos(\mathbf{q}\cdot\mathbf{R}_i + \phi)$$
, and $J_{iy} = A\sin(\mathbf{q}\cdot\mathbf{R}_i + \phi)$.

 $A \equiv$ amplitude factor,

 $\mathbf{q} \equiv$ wave vector which determines the periodicity of the helical structure,

 $\phi \equiv$ arbitrary phase angle.

The ferromagnetic structure is a special case where $\mathbf{q} = 0$. The exchange energy of the structure can be calculated using,

$$E_{ex} = -(g-l)^2 A^2 \sum_{i,j} J(R_{ij}) \cos(\mathbf{q}, \mathbf{R}_{ij})$$

The Fourier Transform of the exchange coupling constant can be defined by,

$$J(\mathbf{q}) = (g-1)^2 \sum_{j} J(\mathbf{R}_{ij}) \exp\left[i\mathbf{q} \cdot \mathbf{R}_{ij}\right]$$



.

Figure 2-10. The magnetic structures of hcp heavy lanthanide metals as revealed by neutron diffraction. The moments in each hexagonal layer are parallel and the diagram indicates how the total moment of each layer is aligned relative to the plane of the layer and how the layers stack up.

then,

$$E_{ex} = -A^2 N J(\mathbf{q}).$$

Thus, the energy of the spin system is a function of the wave vector \mathbf{q} and the most stable configuration is the one whose \mathbf{q} maximises the Fourier Transform $J(\mathbf{q})$ of the exchange constant.

Conduction Electron Polarization [20]

In mediating the indirect exchange coupling between 4f electrons of neighbouring ions, the conduction electrons themselves acquire a net polarization. It has been generally assumed that this polarization is parallel to the 4f moment, accounting for an obvious bulk magnetization in excess of the maximum ionic moment $g\mu_B J$. In the heavy rare earths this excess moment (which amounts to ~4% of gJ in the case of Tb) roughly follows (g - I)J, the projection of the ionic spin onto the total angular momentum, as expected if the s-f exchange and the susceptibility of the conduction electrons remain constant across the series.

However, the validity of this simple picture becomes questionable when the spinorbit coupling of the conduction electrons, which mixes spin-up and spin-down states, is considered. Such a mixing is equivalent to a deviation between the direction in which the conduction electrons are polarized and the direction of the 4f moment. The spin component perpendicular to the magnetization is found to be proportional to a spin-orbit coupling parameter λ_{so} , the s-f exchange and the susceptibility of the conduction electrons. The existence of the perpendicular spin component has been invoked in an explanation of the observed coupling between acoustic magnons and optic phonons in Tb.

2.5 Magnetism in the Rare Earths

The rare earth elements (except Yb and La with empty 4f levels) display magnetic order with a wide variety of spin configurations including complex spin wave structures in the heavy rare earths shown in figure 2-10 [19]. Several of the elements pass through more than one magnetic phase as a function of temperature. The magnetic states of the rare earths are of interest to surface scientists because the well-defined submonolayer structures can be correlated with magnetic behaviour. The ordering temperatures between magnetic states in the rare earths are often close which indicates that surface effects may perturb magnetic configurations. The layer-by-layer growth of rare earths also provides a suitable platform to study the effects of the transition from 2-D to 3-D spin arrangement. The most extensively studied rare earth is Gd with its 7 unpaired 4f electrons and a single ferromagnetic phase with a transition temperature of 293K, the highest of the lanthanides. It is of interest to note that the surface Curie temperature is approximately 20K higher than the bulk value [21] and Gd deposited ono a Fe(001) surface is antiferromagnetically coupled [22, 23].

Neutron Diffraction Investigations of Magnetic Structures. [24]

Gadolinium

The high neutron capture cross-section of naturally occurring Gd creates severe problems for such studies. Nevertheless, Cable and Woollen [25] made a detailed study using a neutron beam of wavelength 0.353Å for which the absorption cross-section is much lower than for thermal neutrons which have a wavelength of approximately 0.9Å. The results indicate that Gd is a ferromagnet at all temperatures below its initial ordering temperature. The generalised susceptibility $\chi(q)$ for the conduction electrons of Gd had a maximum at $\mathbf{q} = 0$ [26] though matrix elements were neglected in their calculations. Lindgård *et al* [27] showed that matrix element effects are important, but still obtained $\mathbf{q} = 0$ as the maximum of $J(\mathbf{q})$.

The ferromagnetic moment in Gd is parallel to the c-axis from T_C (293K) down to 232K and below which moves away from the c-axis reaching a maximum deviation of 65° near 180K. At still lower temperatures it moves back to within 32° of the c-axis. This curious behaviour is due to the temperature variation of the weak single-ion anisotropy constants for Gd. Since Gd is an S-state ion, there is no anisotropy to first order, but higher order effects of the spin-orbit coupling can yield such anisotropy terms.

Terbium

There is an initial ordering to a basal spin plane spiral structure at $T_N=230.2K$. The range of stability of this structure is, however, very narrow and at 225K, a first order transition to a basal plane ferromagnet begins, with a range of approximately 10K where both phases co-exist. There is also some temperature hysteresis. This transition is in agreement with the theory of the magnetoelastic driving force and the ferromagnetic phase is stable down to the lowest temperatures. An ordered moment of $9.0 \mu_B$ /ion was obtained [28] which is consistent with the free ion ground state value as given by Hund's rules. Magnetization measurements show that the easy direction is a b-axis. The ordered moment increases smoothly through the spiral-ferromagnetic transition. The value of q_m increases slightly with decreasing temperature before decreasing as the superzone gaps open up due to the spiral order. q_m then increases again once the mixed phase with ferromagnetic order becomes established.

Magnetization and Susceptibility [20]

In general, the first excited multiplet is sufficiently separated in energy from the ground multiplet that the ion reflects the properties of this latter multiplet alone. In the

crystalline state the electric field from the surrounding ions removes the (2J + I)-fold degeneracy of the ground multiplet, but the crystal field splittings remain much less than the spin-orbit coupling energies (though Sm is an exception in this case). Subject to a number of simplifying assumptions, this two-ion coupling may be considered isotropic and, indeed, many magnetic properties may be interpreted on this basis.

Comparison With Experiment - Terbium

Tb orders ferromagnetically at 220K. The powerful uniaxial anisotropy confines the spins to the basal plane with the $b\langle 10\overline{1}0\rangle$ direction as the easy axis. The saturation moment is somewhat higher than the maximum ionic moment of the ground multiplet, $g\mu_B J = 9\mu_B$. The self-consistent ionic moment J_z was calculated and is shown in figures 2-11a and 2-11b as dotted lines [20].

The moment is slightly quenched by the crystal field and the calculated moment at T=0K is $0.04 \mu_B$ below the $g\mu_B J$ value. The difference between the experimental magnetization curves and the calculated ionic moment is usually attributed to a polarization of the conduction electrons. From the b-direction results, this may be deduced to be $0.33 (\pm 0.05) \mu_B$ /ion in a zero magnetic field at T=4.2K. Allowing for this conduction electron polarization, there is good agreement between the calculated and measured results for both the b- and a- directions.

The temperature dependence of the reduced magnetism m(T, 0) is compared in figure 2-11c [20] with available experimental results. The conduction electron polarization has been subtracted from the measured magnetization using the formula,

$$M_{ce}(T,H) = \chi_{ce}(T) \left[H + \lambda M_{ion}(T,H) \right]$$

with $\chi_{ce}(T) = p + qT^2$

and p=1.4 (± 0.8) $\mu_B T^{-1}$ and q=-3.8 x10-8 $\mu_B T^{-1} K^{-2}$.

To a good approximation, the data may be characterised by the expression [29],

$$\Delta M(T,0) = T^{\frac{3}{2}} \exp\left|\frac{-\Delta}{k_B T}\right|$$

where $\Delta = E_o(T = 0) = 20$ K

In the antiferromagnetic phase (220K < T < 230K), magnetization and neutron diffraction studies indicate that the moments remain in the basal plane and form a spiral structure with a 20° interplanar angle. The narrow temperature range of its existence suggests



Figure 2-11a. The high field magnetization of Tb as a function of internal field in the easy b-direction. The broken lines represent the calculated ionic moment, while the solid lines indicate the total moment per Tb atom. Figure 2-11b. The high field magnetization of Tb as a function of internal field in the hard a-direction. The calculated ionic moment and total moment are shown as broken and solid lines respectively. The symbols represent measurements at 1.8K(+), $4.2K(\bullet)$, 65.5K(O) and $77K(\times)$. Figure 2-11c. The calculated relative magnetization m(T, 0) of Tb together with the experimental results (O). that this structure is energetically weak and in fact an applied field of 1T in the basal plane is sufficient to align the moments ferromagnetically.

Above 230K the susceptibility follows Curie-Weiss behaviour with an effective paramagnetic moment of $9.77 \,\mu_B$ /atom. As a result of the uniaxial anisotropy, the paramagnetic Curie temperatures $\theta_{\parallel C}$ and $\theta_{\perp C}$ are displaced and have the values 195K and 239K respectively.

Comparison With Experiment - Gadolinium.

Since the indirect exchange coupling is between spins, Gd is distinguished among the rare earths by the highest Curie temperature (292.7K) as a result of its $4f^7$ electronic configuration and ${}^{8}S_{7/2}$ ground state. The absence of an orbital contribution to the moment implies that the anisotropic interactions in the equation,

 $H = H_{ex} + H_{an} + H_{el} + H_{me} + H_{Zee}$

arise from perturbations of higher order than have so far been considered. Nevertheless, the residual anisotropy is manifested in the temperature dependence of the easy axis of magnetization. The components of this Hamiltonian comprises of isotropic exchange, effective single-ion anisotropy, elastic, magnetoelastic, and Zeeman terms.

Immediately below T_C , the easy axis is the c-direction. On cooling, at approximately 50K below T_C , the easy axis begins to tilt away from [0001] reaching a maximum cone angle of 60° at 180K before decreasing to just below 30° at 4.2K. Since the angular dependence of the total anisotropy energy is very weak around 200K, local inhomogeneities or strains may readily stabilise the moments in the basal plane [30].

Experiments carried out by Roeland *et al* [31, 32] have investigated the sensitivity of magnetization at a temperature of 4.2K in two samples of Gd – a commercially available single crystal referred to as Gd-A and a single crystal grown in the laboratory referred to as Gd-B in which the oxygen content is reduced to 0.01 atomic per cent with respect to Gd-A in which the oxygen content was a few atomic per cent.

Figure 2-12 illustrates a striking difference in the c-axis magnetization of these two samples [31]. Gd-B saturates in a very small field and may be described as magnetically very soft. This is in contrast to Gd-A in which considerable fields are required to saturate the sample, presumably due to pinning of domain walls by crystal defects. Moreover, the c-axis moment $M_0=7.55 \ \mu_B/a$ tom obtained via the expression $M = M_0 + \alpha B^{-1}$ agrees with a similar analysis for Gd-A and contrasts with the value 7.62 (± 0.01) μ_B/a tom obtained for Gd-B. The anisotropy of the magnetization was estimated to be no more than 0.1%. For the b-direction, $M_0=7.63 (\pm 0.01) \ \mu_B/a$ tom.

This discrepancy between Gd-A and Gd-B may be accounted for by the presence in Gd-A of an oxygen concentration of ~ 2 atomic per cent in the form of Gd₂O₃ which



Figure 2-12. Comparison of the high field magnetization of two Gd crystals. Gd-B was two orders of magnitude purer than Gd-A.

...

saturates in about 20T to $6.9 \mu_B$ /atom. In an attempt to determine the conduction electron susceptibility, Roeland *et al* [31, 32] analysed the Gd-B data using the expression $M = M_0 + \chi B + \alpha B^{-1}$. No evidence for an enhancement over the Pauli susceptibility was found.

The zero-field moment of $7.63 \mu_B$ allows a direct estimate of the conduction electron polarization as $0.63 \mu_B$, since the anisotropy induced zero-point motion is negligible for Gd. This increased estimate of the conduction electron polarization is of particular significance for energy band calculations.

The temperature dependence of the relative magnetization was determined by Nigh *et al* [33]. From 0K to 100K the magnetization decreases with temperature almost twice as fast as does the $S = \frac{7}{2}$ Brillouin function expression owing to the two dimensional character of the spin-wave dispersion relation. Above T_C the susceptibility displays evidence of short range ordering, while above 400K Curie-Weiss behaviour is exhibited with a paramagnetic Curie temperature of 317K and an effective moment of 7.98 μ_B /atom, close to the $g\sqrt{J(J+I)}$ value of 7.94 μ_B /atom.

Magnetic Anisotropy [20]

The strong coupling of the angular momentum L to the large 4f spin S in the presence of a crystalline electric field leads to a giant magnetic anisotropy which is electrostatic origin in most of the lanthanides. At the beginning of the series the large radii of the 4f charge clouds results in an anisotropy which is of comparable magnitude to the exchange energy and directly influences the type of magnetic order. For the elements beyond Gd the anisotropy can be treated to a first approximation as a perturbation on the exchange and only has a small effect on the magnitude of the T=0K moment given by the ground state value J_z . However, the anisotropy does have a pronounced effect on the stable magnetization direction and hence may be elucidated by torque or magnetization measurements which are used to derive the appropriate macroscopic anisotropy parameters. A careful study of the spin-wave energy gap at zero wave vector allows the microscopic analogues to be deduced.

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Chapter 3

Experimental Techniques

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3.1 Summary

This chapter describes the main items of equipment and techniques used to obtain the results presented in this thesis. Since all of the work was undertaken using synchrotron radiation (available from the Synchrotron Radiation Source at the Daresbury Laboratory) a brief summary of the origin is presented at the beginning of the chapter and the need for Ultra High Vacuum (UHV) is explained in section 3.3. All of the preparatory work was carried out at Leicester using the Leicester University Spectrometer for Ions and Electrons (LUSIE); it is described in section 3.4. There follows a description of the sample manipulator, the vapour sources and the LEED/Auger optics. At the Daresbury Synchrotron Radiation Source (SRS) the Surface X-ray Diffraction data was collected an environmental chamber described in section 3.5. A brief description of beamline 9.4 and the 6-circle diffractometer is also given. All photoemission experiments at Daresbury were performed with the peripatetic surface science chamber, SURF1, which is described in section 3.6 together with brief outlines of the liquid helium cooled sample manipulator and the beamlines 1.1 and 5U. The methods of sample preparation are treated in section 3.7.

3.2 Synchrotron Radiation [1]

The Daresbury Synchrotron Radiation Source (SRS) is an electron storage ring consisting of 16 straight sections with bending magnets at the junction of each straight that maintain the electrons in an approximately circular path. As their path is curved by the bending magnet, the electrons undergo radial acceleration causing them to emit electromagnetic radiation. At low energies the emission has a characteristically toroidal pattern (figure 3-1a) [2]. The Daresbury SRS, however, has an operating energy of 2GeV and the electrons orbit the ring at near light speed. In consequence the electrons have relativistic energies and the radiation is emitted in a highly collimated beam at a tangent to the orbital path (figure 3-1b) [2]. The beam is continuous and almost fully linearly polarised in the orbital plane.

For any given orbital of radius r, the critical wavelength for synchrotron radiation is given by, [3]

 $\lambda_{\rm c} = \frac{4\pi r}{3\gamma^3}$

where,

$$\gamma = \frac{1}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} = \text{Emc}^2 = \frac{\text{Bevr}}{\text{mc}^2}$$

The critical wavelength, λ_c , is defined such that half the total power is emitted at wavelengths less than λ_c and half the power is emitted at wavelengths higher than λ_c . The peak intensity occurs at $\lambda \approx 0.7 \lambda_c$.



Figure 3-1. The classical picture for the geometry of synchrotron radiationemission. The angular distribution of emitted intensity from a slow electron on a circular orbit is toroidal (above), but is distorted into a narrow cone in the instantaneous direction of motion (below) for a relativistic electron moving at near light velocity (β =v/c≈1)

The intensity of the emitted radiation can be increased over that of a bending magnet by inserting an undulator into a straight section. An undulator source has all the good properties of a bending magnet (high intensity, highly collimated, plane polarized electromagnetic radiation originating from a small source size) but instead of a broad continuous energy spectrum, the undulator produces very intense light at a fundamental photon energy and a few of its harmonics [4]. An undulator consists of two periodic arrays of magnets. The magnets are aligned with alternating polarity which causes the orbiting electrons to follow a sinusoidal path through the undulator. Electromagnetic radiation is emitted at each point where the electrons change direction, producing very intense emission at the fundamental energy.

Higher energy photons in the X-ray region can be obtained from a wiggler. This insertion device consists of three magnets and the intense magnetic field introduces a 'wiggle' into the electron path. The radius of curvature of the electron path is smaller than in a bending magnet which results in radiation emitted with a much shorter wavelength than that emitted from a conventional bending magnet.

3.3 The Need for UHV

The study of atomically clean surfaces requires an ultra-high vacuum (UHV) environment. Figure 3-2 [5] is derived from the kinetic theory of gases and shows the rate of arrival of a single monolayer of atoms at a surface as a function of pressure. Typical experiments may require data collection over several hours so very low base pressures are necessary to prevent significant contamination.

The kinetic theory of gases shows that the average number of gas molecules striking a unit area of the surface per second is proportional to the pressure,

$$rate = 3 \cdot 51 \times 10^{22} \frac{P}{\sqrt{2\pi mkT}} s^{-1}$$

where P is the pressure in torr, m is the atomic mass and T is the absolute temperature.

Assuming a sticking coefficient of 1 and a 10^{-8} mbar atmosphere of nitrogen gas at 300K, a nitrogen monolayer (approximately 10^{14} atoms cm⁻²) would form within three minutes. Under UHV conditions (P $\leq 10^{-10}$ mbar) the monolayer will take 5 hours to form, long enough to carry out most experiments.

Water vapour in the vacuum system is the main obstacle to achieving UHV. To remove the water vapour it is necessary to heat the whole vacuum system to 150°C for at least 36 hours to thoroughly degas all metal surfaces.



Figure 3-2. Properties of gas under vacuum conditions. The study of atomically clean surfaces requires UHV conditions to minimise contamination.

3.4 Leicester University Spectrometer for Ions and Electrons (LUSIE)

Preliminary sample preparation was undertaken at Leicester in the LUSIE spectrometer. The chamber is made from non-magnetic stainless steel and TIG (tungsten inert gas) welded. The chamber and the pumping ports are lined with two layers of mu-metal which restricts the magnetic field within the chamber to 10 mgauss. All sample preparation and characterisation is carried out at the same level (figure 3-3). A Varian four grid display optics system, incorporating an electron gun, is used for Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES) and Secondary Electron Emission Crystal Current (SEECC) measurements. When measuring AES and SEECC, the LEED optics were controlled by an LSI II/23 computer.

Pressures of $\leq 3x10^{-11}$ mbar are routinely achieved after baking at 150°C for 36 hours. When at UHV, the chamber is pumped by a Varian 400ls⁻¹ triode ion pump and two liquid nitrogen cooled titanium sublimation pumps (TSPs). During initial outgassing and argon ion sputtering, the ion pump is valved off and the TSPs are not cooled. Pumping is provided by an Edwards E04 diffusion pump and liquid nitrogen cooled cryotank with a pumping speed of 680ls⁻¹.

A Vacuum Generators AG2 argon ion gun is permanently mounted on the chamber and is used to sputter clean single crystal substrates. Several ports are available for the mounting of vapour sources. Sample positioning is achieved by a manipulator mounted on the chamber allowing full motion in the x, y and z directions. Polar and azimuthal rotation is also available. The manipulator can be fitted with various sample heaters depending on whether sample preparation requires radiative heating (copper substrates) or electron beam bombardment (molybdenum substrates).

3.4.1 Sample Manipulator

A standard VG UMD20 manipulator gives x, y and z motion with polar and azimuthal rotation. A continuous loop of stainless steel tubing connected internally to a reservoir allows liquid nitrogen cooling of the sample. The electrical connections are made through standard feedthroughs. Depending on the substrate used, the sample heating is achieved either by electron beam bombardment or by radiation.

Radiative Heating

A tungsten filament is threaded through one bore of twin-bore alumina rods and then doubled back along its length through the other bore. The alumina rods are cut to specific lengths and shapes so that the filament can be coiled and then sandwiched between

Plate 1.

Leicester University Specrometer for Ions and Electrons





Figure 3-3. Plan of the experimental layout of the Leicester University Spectrometer for Ions and Electrons (LUSIE). The arrangement allows for LEED and Auger measurements to be taken during deposition.

two recessed molybdenum plates (figure 3-4a). The copper crystal is held in position by two tantalum clips. The copper crystal was cut with step edges on opposite sides of the crystal face so that it could be fixed with face sitting proud of the sample heater.

Electron Beam Bombardment

The cleaning process for molybdenum requires electron beam bombardment to achieve the necessary high substrate temperatures. The Mo crystal needs to be heated to 2100K which is not possible through radiative heating.

The molybdenum crystal was held by tantalum clips onto D-plates fixed to two support legs electrically isolated from earth (figure 3-4b). One of the support legs is connected to a feedthrough so that voltage can be applied to the sample. A spiral filament wound from 0.2mm thoriated tungsten wire was mounted across two other support legs level with the top of a spun tantalum heat shield. The tantalum can also serves to focus the electrons onto the sample. It is important that the filament is level with the top of the tantalum can to ensure uniform heating of the sample.

3.4.2 Vapour Sources

The evaporators (figure 3-5) used are modified Knudsen Cells capable of heating evaporants to ~1300°C [6]. Rare earth metals were supplied in ingot form by Johnson Mathey of Royston and are of a nominal 99.999% purity. The metal was placed in a tantalum lined alumina crucible. A tungsten filament is wound round the alumina crucible and the whole assembly is enclosed inside a water cooled shroud. The temperature of the evaporant is monitored via a chrome-alumel thermocouple attached to the tantalum liner. A shutter covers the aperture and is operated by means of a rotary drive. When fully outgassed, the chamber pressure during deposition can remain in the low 10^{-10} mbar range.

3.4.3 Low Energy Electron Diffraction (LEED)

Because of wave-particle duality, electrons with wavelengths comparable with the dimensions of a regular crystal will be diffracted. Interference between diffracted electrons will produce a diffraction pattern that represents the reciprocal lattice of the crystal.

So, the electron beam energy required for LEED is determined by the crystal layer spacing.

$$E = \frac{p^2}{2m} = \frac{1}{2m} \frac{h^2}{\lambda^2}$$

For $\lambda \sim d=1$ Å, E~150eV.



Figure 3-4. Above: SXRD sample heater used for electron beam heating of Mo(110) crystals. Below: The radiative heater used to heat the Cu(001) sample.



Figure 3-5. Schematic diagram of the vapour source with the cryoshield sectioned.

The Varian standard four grid LEED optics consists of four concentric grids and a fluorescent screen (figure 3-6). Each of these has a central aperture through which passes the electron gun. In operation, the incident electron beam is typically a few hundred eV and the sample is earthed. Grids G1 and G4 are earthed while grids G2 and G3 have a slightly lower potential than the beam energy to suppress inelastically scattered electrons. The phosphor-coated screen has a high positive voltage of 6kV which accelerates the electrons causing fluorescence on the screen. The resulting LEED pattern is viewed through the window opposite the LEED optics. A fuller description is given in §4.4.

3.4.4 Auger and SEECC

The Varian LEED optics can be used as a retarding field analyser to detect electrons. In this case, the electron gun produces an electron beam of much higher energy than that used for LEED, typically 2.5kV. The electron beam is incident on the sample and produces a reflected current of elastic and secondary electrons consisting primarily of Auger electrons and electrons which have suffered an inelastic energy loss. The Auger electrons arise when an ion emits an electron from its valence band with energy provided by the decay of another electron into the core hole. The energy of the emitted electron is independent of the energy of the ionising radiation and characteristic of the element and the intensity of an Auger peak provides a measure of the occurrence of a given element.

A ramped negative voltage (V_E) with superimposed modulation voltage (ksin(ωt)) is applied to grids G2 and G3. The current reaching the screen (collector) is given by,

$$I(E) = I(V_E) + k.N(E).sin(wt) + \frac{k^2}{4} \frac{dN(E)}{dE} [1 + cos(2wt)]$$

where N(E) = the energy distribution of the electrons leaving the sample.

It follows from the equation that N(E) is measured by detecting the component of I(E) at ω , while $\frac{dN(E)}{dN}$ is measured at 2ω .

The differentiated Auger signal can be measured by halving the modulation frequency while detecting the current at the original frequency using a tuned pre-amp and phase-sensitive detector. The LSI II/23 computer controls the ramp energy and input of the phase-sensitive detector signal allows the Auger spectra to be displayed. To negate pick-up between the grids and the screen, a neutralizing capacitor is introduced into the circuit inside the 'mixing box'.

Auger electron spectroscopy (AES) measurements are made with the computer scanning over the required energy range, plotting the differentiated Auger signal. AS-t measurements are taken using the same arrangement, but the computer program scans a small energy range repeatedly. Parameters are set within the program to scan the strongest



Auger peaks of the substrate and/or adsorbate. The first scan gives the reference peak-topeak value (I₀) and subsequent scans are plotted relative to this value.

SEECC measurements are made by measuring the sample drain current as a function of time during deposition with a high energy electron beam incident on the sample [7, 8]. The drain current is measured by earthing the sample through a Keighley current amplifier with a typical gain of 10^7 . This is treated later in §4.3.

3.5 Leicester University X-Ray Chamber - LUXC.

All surface X-ray diffraction measurements were taken using the purpose-built UHV chamber. The main chamber consists of a stainless steel tube, on one end of which is mounted the sample manipulator and on the other is a rear view LEED system. There are a number of ports, all facing towards the sample, which accommodate the surface science apparatus (figure 3-7).

Mounted on the chamber are a Vacuum Generators LEG31 electron gun and VSW HA50 hemispherical analyser used for Auger electron spectroscopy (AES and AS-t). A 0-10kV argon ion gun is used to sputter clean the samples. Ports are available for up to four evaporators/vapour sources and a VG SX200 residual gas analyser.

Incident and scattered X-ray beams pass through the 200°x30° beryllium window which is welded into the wall of the chamber, close to the sample position.

Once UHV is achieved after baking the system for 24 hours at 150°C, the chamber is pumped by a Varian 400ls⁻¹ ion pump and liquid nitrogen cooled titanium sublimation pump (TSP). During initial outgassing and argon ion sputtering, the ion pump is valved off and the chamber is pumped by a 400ls⁻¹ Balzers turbo molecular pump. A base pressure of $3x10^{-11}$ mbar is routinely achieved.

3.5.1 SXRD sample manipulator

In the LUXC chamber, the single crystal substrates are mounted on a sample manipulator which is connected to a differentially pumped rotary seal and bellows (figure 3-8). These allow for the rotation of the sample in the UHV chamber which is essential for X-ray diffraction.

The rotary feedthrough was made at Leicester University. A highly polished stainless steel tube rotates inside three viton sealing rings which separate the two differentially pumped stages. The low vacuum stage is pumped by a rotary pump while the high vacuum stage is held at 10^{-6} mbar by a small 50ls⁻¹ Balzers turbo molecular pump. It is possible to rotate the feedthrough through 360° without measurable leakage between the UHV chamber and the high vacuum stage of the feedthrough. The chamber and the



Figure 3-7. The Surface X-ray Diffraction chamber shown coupled to the diffractometer on beamline 9.4 at the Daresbury SRS. Also shown is the assembly for the out-of-plane measurements.



feedthrough are connected by a bellows allowing azimuthal rotation of $\pm 15^{\circ}$. Normally the feedthrough is connected to the ϕ axis of the diffractometer.

The sample heater has been designed and built at Leicester University specifically to allow for sample transfer. The heater sits in a stainless steel tube at the end of the rotary feedthrough. Samples are held in place by tantalum clips with the single crystal samples cut with step edges such that the surface stands proud of the sample holder. This eliminates 'shadowing' of the X-rays by sample heater components. The sample is electrically isolated from earth allowing the application of high voltage during electron beam bombardment. A spiral filament sits directly behind the sample and is wound from 0.25mm thoriated tungsten wire. The body of the sample heater is earthed through a large rectangular copper peg which also locates the sample heater in the rotary feedthrough during sample transfer and also provides a heat transfer path for sample cooling.

3.5.2 Beamline 9.4 - Surface X-Ray Diffraction

Station 9.4 at Daresbury Laboratory [9] uses hard X-rays produced from a wiggler inserted into a straight section of the storage ring, the wiggler consisting of three liquid helium cooled 5 Tesla superconducting magnets. The radius of curvature of the electron path is smaller in the wiggler than within a bending magnet and the intense magnetic field introduces a wiggle into the electron path. This results in radiation being emitted from the wiggler which has a shorter critical wavelength than radiation emitted from a conventional bending magnet and a higher intensity for X-rays of wavelengths of the order of 1Å.

There is a 63mrad fan of X-rays emitted from the wiggler and the beamline optics select only the central 4mrad. A doubly focussing, toroidal mirror at 18.2m from the source focusses the X-rays onto the sample (at 38.0m). The wavelength of the radiation can be selected using the water-cooled, channel-cut Si(111) monochromator.

A small air-filled ion chamber positioned after the final slits and before the UHV chamber normalises the measured reflected X-ray signal to variations in the intensity of the incident beam.

The beam passes through the beryllium window on the UHV chamber, is incident on the sample and the scattered radiation passes out through the opposite side of the beryllium window and is collected by the liquid nitrogen cooled, solid state germanium detector. Between the UHV chamber and the detector there are two sets of four jaw slits that collimate the scattered beam and define the resolution. These two sets of slits are separated by a rigid pipe which has mylar windows at each end and is either evacuated or filled with helium gas to reduce air scattering.

The detector operates up to a maximum of $\sim 5x10^4$ counts s⁻¹ and the background (with the sample moved out of the beam) is typically 0.1 count s⁻¹.

3.5.3 Six-Circle Diffractometer

Figure 3-9 is a schematic representation of the six-circle diffractometer in use on station 9.4. It is, essentially, a standard four-circle diffractometer mounted on a rotary table providing the fifth circle. A sixth circle has been introduced by the addition of a mounting for moving the detector 15° out of plane [10]. The detector is fixed in the mounting and can be moved between two positions, $\gamma=0^{\circ}$ and $\gamma=15^{\circ}$. The detector is moved manually between the two positions while all the other circles are driven by DC motors with optical encoders measuring their precise positions. Each motor has eight thousand steps per degree allowing smooth and precise positioning. Each motor is controlled by individual electronic computers with feedback to ensure smooth and efficient movement.

3.6 Daresbury Surface Science Chamber, SURF1.

All photoemission measurements made at Daresbury SRS were collected in the peripatetic SURF1 chamber. This chamber is made from stainless steel and is lined with two layers of mu-metal to keep the magnetic field below 10mgauss. Several ports are available for the mounting of vapour sources, LEED system, electron gun, argon ion gun and HA150 analyser for the collection of photoelectrons. The ports are arranged such that deposition may be made and photoemission measurements can be taken without moving the sample and so reduce lag time between deposition and measurement and minimise contamination.

After baking at 150°C for 36 hours, the chamber is pumped by a Varian 400ls⁻¹ water-cooled turbomolecular pump and with a liquid nitrogen cooled titanium sublimation pump a base pressure of 6×10^{-11} mbar was routinely obtained.

3.6.1 Liquid Helium Cooled Sample Manipulator

The sample manipulator used at Daresbury SRS consisted of a standard Vacuum Generators HPLT series xyz table with a differentially pumped rotary feedthrough and an Oxford Instruments CF1100 special continuous flow cryostat. The differentially pumped rotary feedthrough allows 360° axial rotation as the helium entry is along the manipulator axis and there is the normal range of movement in the x, y, and z directions. However, the sample could not be rotated azimuthally about the surface normal of the sample because of the size limitations imposed by the radiation shield and an azimuthal drive would result in a poorer thermal path between the heat exchanger and the sample which would limit the base temperature of the cryostat. Samples could be cooled from room temperature to 100K within 30 minutes and a base temperature of 80K was achieved within one hour after which the rate of flow of the liquid helium could be reduced to between 1 and $1.5 \, \text{lm}^{-1}$ and still maintain the



Fig 3-9. Schematic diagram of the six circle diffractometer on station 9.4 at the Daresbury SRS.

Plate 2

Daresbury NEXAFS Chamber



base temperature. This chamber and manipulator were used for experiments on two beamlines – station 1.1 and station 5U.

3.6.2 Beamline 1.1

Station 1.1 [11] provides soft X-rays in the energy range 250-1200eV. It was designed for NEXAFS (Near Edge X-ray Absorption Fine Structure) since the energy range encompasses the K edges of carbon, sulphur and oxygen, but it has been modified to provide circularly polarized light for MCD experiments. The beamline is also used for standard photoemission measurements.

Radiation from the storage ring is deflected and focused by a Pt-coated SiC premirror on to the High Energy Spherical Grating Monochromator (HEGSM). There are three gratings (1050, 1500 and 1800 lines mm⁻¹) to provide the full energy range of 250-1200eV. The beam is deflected onto the sample by a Pt-coated spectrosil ellipsoidal mirror. The specification of the beamline is a flux of approximately $2x10^{11}$ photons s⁻¹, 0.3% bandwidth and a beam size of 1x1mm at the sample.



Figure 3-10. Rotation of the chopper selects left or right circularly polarised light from either the upper or lower portion of the beam.

Circularly polarised light can be selected by inserting a chopper into the beamline. The chopper, as shown in figure 3-10, is a cylinder with horizontal slots in the top and bottom at right angles to each other and it is directly in front of the monochromator allowing selection of light of either helicity. An obscuration plate is driven into the beam to block the central portion of the beam (the central 0.1-0.2 mrad) and two beams are created; one from above the orbital plane and the other from below. These beams impinge on the chopper which is rotated on its vertical axis to select helicity, that is allow only either the top or lower half of the beam to be transmitted.

Synchrotron radiation emitted from a bending magnet is linearly polarized only in the plane of the storage ring, but out of plane the light becomes elliptically polarized. So, radiation at the sample is linearly polarized only as the vertical aperture becomes vanishingly small. By blocking the central portion of the beam, it is possible to allow only the upper or lower portion of the beam to be transmitted to the sample. In this way circularly polarized light is obtained, but at the expense of photon flux. The degree of circular polarization is 0.75-0.8 depending on the grating used.

3.6.3 Beamline 5U

This station has an SX700 type plane grating monochromator with no entrance slits [12-14]. There is a spherical focussing mirror and a 6m exit arm to an ellipsoidal postfocussing mirror. The monochromator is a single grating with 1200 lines mm⁻¹ and covers the photon energy range of 80-1000eV. This is the only beamline at Daresbury SRS with an undulator source. It consists of a 1m array of permanent magnets with a gap that is variable between 42 and 88mm. An undulator source has the best properties of a bending magnet source, that is high intensity, highly collimated beam and plane-polarized radiation. Instead of a broad continuous energy spectrum, the undulator produces very intense radiation at a fundamental photon energy and a few of its harmonics. The magnetic field within the undulator determines the fundamental photon energy and this can be varied by changing the separation between the two arrays of magnets [4]. In practice, at higher energies, it is operated at minimum gap, where harmonic radiation produces a quasi-continuous output extending from the first harmonic at 60eV to beyond the upper operating limit of the monochromator. The advantage of an undulator is the increased photon flux that is provided allowing for better counting statistics. However, for the work presented here, radiation of energy 600eV was used and the photon intensity at these energies is not so high as at the low energy end of the undulator range, but the flux is still higher than for radiation from a simple bending magnet.

3.7 Sample Preparation

Two different single crystal substrates were used in this work, Cu(001) and Mo(110). These two metals require different preparation techniques. The samples were supplied as single crystal boules of 5N (99.999%) purity by Metal Oxides and Crystals of Cambridge. Each of the samples was cut to the required dimensions and to within 0.2° of their orientation by the School of Metallurgy and Materials at the University of Birmingham.

3.7.1 Molybdenum.

Initially the samples were mechanically polished using progressively finer grades of diamond grinding paste (down to 4 μ). Following thorough degreasing in acetone and methanol ultrasonic baths, the samples were electropolished in a methanol/sulphuric acid mixture [see Appendix A]. The sample was then mounted on a sample heater for UHV cleaning. Under vacuum, the samples were annealed for between 12 and 18 hours at 1300K in an atmosphere of ~1x10⁻⁷ mbar of oxygen. This procedure drives carbon and sulphur from the bulk and leaves a thick oxide layer on the surface. This surface oxide is removed by heating the Mo crystal to a temperature of 2100K for 20-30s. This 'flashing' is repeated until no carbon, sulphur or oxygen are detectable by AES. Subsequent cleaning (for example after deposition) requires only two or three flashes to 2100K.

To achieve the temperature required for annealing and flashing, electron beam bombardment of the sample is necessary. A positive voltage is applied to the sample while the filament is nominally at earth potential. The power requirements for these temperatures are,

(a) 800V, filament current ~5.5A, emission ~35mA for 1300K,

(b) 1500V, filament current ~6.5A, emission ~150mA at 2100K.

The temperatures were measured using a tungsten-rhenium thermocouple fixed securely to the sample.

3.7.2 Copper

Initially the samples were mechanically polished using progressively finer grades of diamond grinding paste (down to 4μ). Following thorough degreasing in acetone and methanol ultrasonic baths, the samples were electropolished in orthophosphoric acid. The single crystal was thoroughly degreased in acetone and methanol ultrasonic baths before mounting under UHV.

Under vacuum, the crystal was cleaned by repeated cycles of argon ion bombardment in an argon atmosphere of 1×10^{-5} mbar with a 1kV argon beam for 30 minutes
followed by annealing to 900K for 10 minutes. This sputter and anneal cycle was repeated • until no contaminants were present on the copper surface.

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Chapter 4

Analysis Techniques

- 4.1 Summary
- 4.2 Auger Electron Spectroscopy
- 4.3 Secondary Electron Emission Crystal Current
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References

4.1 Summary

To study metal surfaces and ultrathin overlayer structures it is necessary to use experimental probes which are surface sensitive. The most important factor in surface sensitivity is the energy used. For example, Auger electron spectroscopy and photoemission require the detection of electrons with energies less than 1keV. Electrons with these energies have an inelastic mean free path of 5-10Å (figure 4-1) and must originate in the top few atomic layers of the sample.

X-ray reflectivity is also shown to be highly surface-sensitive, but only with the geometry of the sample and detector such that detection occurs at the position for destructive interference – the anti-Bragg position. Auger electron spectroscopy and X-ray reflectivity are used to measure adlayer growth in situ.

4.2 Auger Electron Spectroscopy

X-ray photons or high energy electrons, of typically 2.5kV, are fired at the sample to be studied. These incident electrons cause the emission of a core level electron and the resulting hole is filled by the decay of an electron from a higher energy level. This is shown schematically in figure 4-2 where electrons are represented by circles and holes by squares.



Figure 4-2. Schematic diagram of the Auger Process





The net energy gained by this event is sufficient to cause the emission of a second electron from the atom (usually from the valence band or an energy level close to the valence band).

On an elementary level, the kinetic energy of the Auger electron is given by, $E_k = E_H - E_D - E_A$ and it can be seen that the kinetic energy of the Auger electron is independent of the incident electron or photon energy. E_k is a characteristic only of those energy levels involved in the process. Hence each element emits Auger electrons with unique kinetic energies. So, Auger electrons can be used to identify elements, i.e. an atomic fingerprint. Since Auger electrons arise from decays between different energy levels, and each atom can emit Auger electrons with several kinetic energies, it is necessary to adopt a nomenclature to identify the electrons and the processes that lead to their emission. The convention used is $H_x D_y A_z$, where H denotes the shell of the original core hole (K, L, M, etc.), the hole is filled by an electron decaying from shell D and the Auger electron is emitted from shell A. Decay and/or emission can occur from the valence band and in this case the electron shell is labelled V. x, y and z represent the subshells of the energy shells involved, for example $H_x \equiv L_1 = 2s$, $D_y \equiv L_{2,3} = 2p$. (There is usually no differentiation between $2p_{1/2}$ and $2p_{3/2}$). However, the simplistic treatment given above is insufficient because with the creation of the core hole there is a redistribution of charge within the atom which influences the kinetic energy of the ejected electron. A more accurate expression for the kinetic energy of the Auger electron is,

$$E_{HDA}(Z) = E_H(Z) - \frac{1}{2} \left[E_D(Z) + E_D(Z+I) \right] - \frac{1}{2} \left[E_A(Z) + E_A(Z+I) \right]$$
(4-1)

where Z is the atomic number of the element.

Standard tables of Auger spectra exist which are used to identify Auger peaks and by comparing the peak intensities of two peaks (for example Mo at 186eV and O at 510eV) a measure of surface contamination can be calculated.

The width of an Auger peak is dependent on the energy levels involved. For example, if the Auger electron is emitted from the valence band, the width of the peak will be of the order of the width of the valence band (up to 6eV). If the final state has two holes in the valence band, the Auger peak will be broader still. Lifetime broadening also contributes to the peak width. Consider a transition time of $\Delta t \sim 10^{-15}$ s between quantum states. Using $\Delta E \cdot \Delta t \sim \hbar$ gives an uncertainty in the energy of ~0.6eV. This makes little difference to width of Auger peaks, but if one of the final state holes is in the same shell as the initial core hole (a Coster-Kronig transition), the strong overlap of the radial wavefunctions of orbitals in the same shell means that Δt is shorter which leads to Auger peaks that can have widths of tens of eV. Δt is even smaller (and hence the peak is broader) if both the final state holes are in the same state as the initial hole - the Super Coster-Kronig transition. To ease

identification of the positions of the Auger peaks, the spectrum is usually differentiated [1, 2]. The peak-to-background ratio is enhanced in this way.

4.3 Secondary Electron Emission Crystal Current, SEECC.

Inhomogeneities and reconstructions at a metal surface can be detected by measuring changes in the net current i_{cc} flowing in or out of the sample which is bombarded with an electron beam with a chosen energy [3, 4]. Changes in the crystal current effectively reflect changes in the secondary electron emission, which in turn reflects changes in the surface composition and structure.

The technique is simple and inexpensive to implement. An electron beam is incident on the sample and the crystal current is measured by an ammeter through which the sample is earthed. The crystal current varies in both intensity and sign as a function of the energy of the incident electron beam (figure 4-3a, [4]) and the plot is modified by changes at the surface. For example, by the addition of an adsorbate. For varying thicknesses of the adsorbate, a series of parallel curves is obtained which leads to the conclusion that the deposition can be monitored by measuring the crystal current at fixed electron beam energy, particularly at one of the crossover point, Ezcc, where the crystal current is zero for a clean substrate. It has been noted [4] that this procedure does not require a particularly well stabilised electron beam current if the changes are monitored at E_{ZCC} , though the technique is at its most sensitive to changes in the surface structure. It is expected that by concentrating on changes in i_{CC} during deposition of an adsorbate material, one will observe incremental or linear effects of surface composition and any changes in the linearity are due to changes in the surface structure (figure 4-3b) and the formation of submonolayer structures. For alkali metals deposited onto transition metal substrates [3, 4, 5] it was found that the completion of a monolayer corresponded to a maximum in the icc curve, but the maximum in icc corresponds to a submonolayer structure for the deposition of rare earths [6, 7].

The cause of the changes in the value of i_{CC} during the deposition of an adsorbate is still uncertain, but it has been suggested [3] that the enhancement of the secondary electron emission may be due to the increase in surface ionization. Such an enhanced surface ionization might occur due to surface modes of electron scattering induced by the presence of the adsorbed layer. In a simple scheme, the effect per adatom would need to be lower for a condensed adlayer island than for dispersed (isolated) adatoms, thus leading to premonolayer breaks. The effect of a second layer, and of disorder, would be to reduce the effects of the scattering at the adsorbate-substrate interface. Another cause could be that the crystallinity of the surface layers may have an influence on the electron scattering and diffraction at different stages in the adlayer growth; that is, the reflection of the primary beam and the creation and emergence of the secondary electrons.

Plots of i_{CC} as a function of deposition time also show marked distinctions between different adsorbate-substrate systems. For a variety of systems this technique has been



Figure 4-3a. Variation of the secondary electron emission crystal current (SEECC) as a function of incident beam energy.



Figure 4-3b. For a fixed incident beam energy, the crystal current varies in intensity during deposition of an adlayer.

shown to be very sensitive to changes in the structure of an adsorbed layer, such as submonolayer transitions, completion of a monolayer and surface disorder. Features in the i_{CC} plots can be directly related to breaks in AS-t plots and to features of plots showing the changes in work function during deposition, and hence be linked to the formation of submonolayer structures or the completion of adlayers.

4.4 Low Energy Electron Diffraction, LEED.

Since a single crystal is a periodic array of atoms, it is possible to produce a diffraction pattern using X-rays with a wavelength comparable to the interatomic spacing. And using the principle of wave-particle duality, electrons can be treated as a wave leading to the possibility of electron diffraction. Classically, the energy of an electron is related to its momentum by the relation,

$$E = \frac{p^2}{2m} \tag{4-2}$$

From quantum theory, $p = \frac{h}{\lambda}$, this means that $E = \frac{1}{2m} \cdot \frac{h^2}{\lambda^2}$.

So, since interlayer spacing is of the order of 1Å, substituting λ =10⁻¹⁰m gives E≈150eV.

This technique was first shown in 1927 by Davisson and Germer [8]. From the plot by Seah and Dench [9] (figure 4-1), comparing the electron inelastic mean free path versus energy, shows that electrons of this energy will have an inelastic mean free path of 5-10Å making them extremely surface sensitive. For diffraction to occur, the Laue Conditions must be satisfied by the emerging beams and this can be visualised using an Ewald sphere (figure 4-4).

The radius of the Ewald sphere is $|\mathbf{k}|$ and is thus related to the beam energy.

$$E = \frac{1}{2m} \frac{h^2}{\lambda^2}$$
 and $k = \frac{2\pi}{\lambda}$, so substituting for λ gives, $E = \frac{\hbar^2 k^2}{2m}$.

The diffraction conditions are satisfied at each point where the Ewald sphere intersects with the reciprocal lattice rods. The rods are labelled (hk), relating to the reciprocal net of the surface which is given by $g_s=ha^*+kb^*$, where a^* and b^* are the reciprocal lattice vectors. Geometrically, for a rod (hk), wavelength λ , scattering angle 20 (the angle between incident and scattered beams) then,

$$a = \frac{\sqrt{(h^2 + k^2)}.\lambda}{\sin(2\theta)} \tag{4-3}$$



Figure 4-4. The Ewald sphere construction for an incident electron normal to the crystal surface.

So, a plot of $sin(2\theta)$ versus λ will yield a value for *a*, the real space surface unit cell lattice vector.

LEED patterns manifest themselves as a geometric array of bright dots against a diffuse background and the pattern is a direct representation of the reciprocal lattice. Further analysis is possible by measuring the intensity profile of the beams, the technique being known as LEED I-V. The I-V plot consists of a measure of a particular diffraction spot's intensity as a function of beam energy. Comparisons can be made with calculated spectra to give information on surface relaxation and registry between the substrate and the adsorbate. The intensity profile is very difficult to analyse because the cross-section for elastic scattering at a single atom is high for low energy electrons. And calculations are very computer-intensive and are usually only used for clean surfaces and simple overlayer systems.

4.5 X-ray Scattering [10]

(i) The Thompson Formula describes the amplitude, A, of a wave that comes from a scattering atom at \mathbf{r}_e as a function of the amplitude, A₀, of the incident wave and assuming the dipole approximation.

$$A.\exp[-i\mathbf{k}_{f}\cdot\mathbf{r}_{e}] = A_{o}\frac{e^{2}}{mc^{2}}\cdot\frac{1}{R_{o}}\exp[-i\mathbf{k}_{i}\cdot\mathbf{r}_{e}]$$
(4-4)

The $\frac{1}{R_0}$ term arises because a spherical wave is produced when a plane wave is incident.

 e^{2}/mc^{2} has a small value (3×10⁻²⁵m), so even with a large number of electrons in the crystal, the total scattering cross-section is still quite small. Thus, the kinematical approximation is valid, in which case the amplitude scattered by an object can be taken as the sum of independent contributions from all the individual electrons.



Figure 4-5. Definition of the real space vectors used in equations (4-4)–(4-13). Point O is the origin of the crystal, point A is the origin for the nth cell, point B is the jth atom of the nth cell and point C is an electron belonging to the jth atom.

The momentum transfer between the incoming (\mathbf{k}_i) and outgoing (\mathbf{k}_f) waves is \mathbf{q} , where $\mathbf{q}=\mathbf{k}_f-\mathbf{k}_i$. For elastic scattering, $|\mathbf{k}_i|=|\mathbf{k}_f|=|\mathbf{k}|=2\pi/\lambda$. This leads to a derivation of a form of Bragg's Law,

$$|\mathbf{q}| = 2|\mathbf{k}|\sin\left(\frac{2\theta}{2}\right) \tag{4-5}$$

Equation (4-5) is expressed in terms of 2θ since it is the experimental scattering angle.

Equation (4-4) can be rearranged in terms of momentum transfer,

$$A = A_o \frac{e^2}{mc^2} \frac{1}{R_o} \exp[i\mathbf{q} \cdot \mathbf{r}_e]$$
(4-6)

The results of a scattering experiment can be thought of as a map in momentum space, where q is the independent variable and the scattered intensity is the dependent

variable. In general, the sample has three degrees of orientational freedom and the scattering angle is the fourth. A 4-circle diffractometer is used to position the sample and detector in this geometry. This has four concentric circular motions, three of which (ω, ϕ, χ) move the sample to the particular direction of q, and the fourth circle moves the detector by an angle of 2θ , setting the magnitude of q.

Equation (4-6) is the scattering amplitude from a single electron. The kinematical approximation is used to sum the scattering amplitudes from each electron [10].

(ii) The electrons can be represented as density distributions as described by their wavefunctions. So the summation over the electrons now becomes an integral over electron densities.

$$A = A_o \frac{e^2}{mc^2} \frac{1}{R_o} \int_{-\infty}^{+\infty} \rho(\mathbf{r}') \exp\left[i\mathbf{q} \cdot (\mathbf{R}_n + \mathbf{r}_j + \mathbf{r}')\right] d^3 \mathbf{r}'$$
$$A = A_o \frac{e^2}{mc^2} \frac{1}{R_o} f(q) \cdot \exp\left[i\mathbf{q} \cdot (\mathbf{R}_n + \mathbf{r}_j)\right]$$
(4-7)

where f(q) (=f(|q|)) is defined as,

$$f(q) = \int_{-\infty}^{+\infty} \rho(\mathbf{r}') \exp[i\mathbf{q} \cdot \mathbf{r}'] d^{3}\mathbf{r}'$$
(4-8)

f(q) is the *atomic form factor* and is defined as the Fourier Transform of the electron density for a single atom. The atomic form factor is written as a function of the magnitude of the momentum transfer, independent of direction, because in almost all cases the atom is spherically symmetric. More strictly, f(q) is complex and energy-dependent because the X-ray can excite atomic transitions. f(q) is a tabulated function for all atoms in the periodic table.

(iii) The contributions of all the atoms in one unit cell of the crystal can be summed. Since the atoms may not be all of the same element, they must be distinguished by assigning separate atomic form factors $f_j(q)$.

So for N atoms in a unit cell,

$$A = A_o \frac{e^2}{mc^2} \frac{I}{R_o} \sum_{j=1}^N f_j(q) . \exp\left[i\mathbf{q} . (\mathbb{R}_n + \mathbf{r}_j)\right]$$

$$\mathbf{A} = A_o \frac{e^2}{mc^2} \frac{I}{R_o} F(q) \exp[i\mathbf{q} \cdot \mathbf{R}_n]$$
(4-9)

where F(q) is defined as,

$$F(q) = \sum_{j=1}^{N} f_j(q) \exp\left[i\mathbf{q} \cdot \mathbf{r}_j\right]$$
(4-10)

 $F(\mathbf{q})$ is the *structure factor*, a sum over all the atoms in the unit cell. $F(\mathbf{q})$ depends on the direction of \mathbf{q} as well as the magnitude because the relative positions of the atoms are important. In equation (4-10), the structure factor is defined in terms of $f(\mathbf{q})$, but it is sometimes convenient to consider $F(\mathbf{q})$ in terms of the electron density, $\rho(\mathbf{r})$, of one unit cell.

 $\rho(\mathbf{r})$ is defined as the sum of contributions from all atoms in the unit cell,

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} \rho_j (\mathbf{r} - \mathbf{r}_j)$$
(4-11)

So, the structure factor can be rewritten as,

$$F(\mathbf{q}) = \int \rho(\mathbf{r}) \cdot exp[i\mathbf{q} \cdot \mathbf{r}] d^3 \mathbf{r}$$
(4-12)

This is the Fourier Transform of the electron density for one unit cell of the crystal.

(iv) 3D Diffraction

In order to calculate the diffraction from a whole crystal, the sum must extend over all the unit cells. It is at this stage where scattering becomes highly focused along certain directions. Assuming the crystal is cuboid with N1, N2, and N3 unit cells along the three crystal axes which are defined by the vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 , the phase factors for the positions of the origins of the unit cells may be summed,

$\mathbf{R}_{n} = n_{1}\mathbf{a}_{1} + n_{2}\mathbf{a}_{2} + n_{3}\mathbf{a}_{3}$

and this leads to

$$A = A_o \frac{e^2}{mc^2} \frac{1}{R_o} F(\mathbf{q}) \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} \exp[i\mathbf{q}.(n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3)]$$
(4-13)

This expression is just a geometric sum and is the same for all crystals. Any chemical information is contained in the structure factor.

Just one of the sum terms can be used as a basis for deriving all the important properties of diffraction and the other sum terms can be included later.

Consider the identity, $S_N(x) = \sum_{n=0}^{N-1} \exp[ixn] = \frac{1 - \exp[ixN]}{1 - \exp[ix]}$

If we substitute x = qa, this complex quantity represents a simplified version of the scattering amplitude for a one-dimensional crystal containing N atoms. But, experimenters are more interested in $|S_N(x)|^2$ representing the scattered intensity.

$$\left|S_N(x)\right|^2 = \frac{\sin^2(\frac{1}{2}Nx)}{\sin^2(\frac{1}{2}x)}$$
(4-14)

This is also called the N-slit interference function, and equation (4-13) can be rewritten in terms of these interference functions.

$$A = A_o \frac{e^2}{mc^2} \frac{1}{R_o} F(\mathbf{q}) \cdot S_{NI}(\mathbf{q}.\mathbf{a}_I) \cdot S_{N2}(\mathbf{q}.\mathbf{a}_2) \cdot S_{N3}(\mathbf{q}.\mathbf{a}_3)$$
(4-15)

The large N limit $(N \to \infty)$ for a crystal has sharp peaks in $S_N(x)$ at $q = 2\pi \frac{m}{a}$ where m is an integer. In this $N \to \infty$ limit, $S_N(x)$ is a periodic array of δ -functions with a spacing of $\frac{2\pi}{a}$.

This shows that the diffracted intensity from a crystal is along specific, well-defined directions. The generalisation to 3 dimensions, with momentum transfer in terms of the unit cell vectors, leads to the concept of a reciprocal lattice. The diffracted intensity is the product of three orthogonal, periodic δ -function arrays and for the intensity to be at a maximum, 3 separate conditions must be simultaneously satisfied. These are the Laue Conditions,

 $\mathbf{q}.\mathbf{a}_1=2\pi\mathbf{h}$ $\mathbf{q}.\mathbf{a}_2=2\pi\mathbf{k}$ and $\mathbf{q}.\mathbf{a}_3=2\pi\ell$.

and these three conditions are satisfied by the vector,

$$\mathbf{q} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3,\tag{4-16}$$

where,
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$
, $\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$, $\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$.

4.6 Reflectivity and Growth Monitoring [11]

If a plane wave, $e^{i\mathbf{k}\cdot\mathbf{r}}$ is incident on a 'stack' of N atomic layers (figure 4-6a), the momentum transfer is given by $\mathbf{q}=\mathbf{k}_f-\mathbf{k}_i$, where \mathbf{k}_f and \mathbf{k}_i are the wave vectors of the exiting and incoming beams. \mathbf{q} can be separated into 3 components,

$$\mathbf{q}=\mathbf{q}_{\mathbf{x}}+\mathbf{q}_{\mathbf{y}}+\mathbf{q}_{\mathbf{z}},$$

When $q_x = q_y = 0$, the wave is specularly reflected and kinematic diffraction theory gives the scattered wave as,

$$\Psi = \int_{\substack{all\\layers}} \rho(\mathbf{r}) \cdot exp[-i\mathbf{q} \cdot \mathbf{r}] \cdot exp\left[\frac{-z}{\mu}\right] \cdot d\mathbf{r}$$

The exp[-z/ μ] term accounts for the decay of the beam as it enters and leaves the sample. Summing over all N layers (N»1) and using the primitive lattice vectors (considering only the z-direction, since ($q_x = q_y = 0$) gives,

$$\Psi = \sum_{n=0}^{N-I} F(q_z) \exp\left[-n(iq_z a_3 + \frac{a_3}{\mu})\right]$$
(4-17)

But using the identity, $\sum_{n=0}^{N-1} e^{nx} = \frac{1 - e^{Nx}}{1 - e^x}$

leads to,

$$\psi = F(q_z) \cdot \frac{1 - \exp\left[-N(iq_z a_3 + \frac{a_3}{\mu})\right]}{1 - \exp\left[-(iq_z a_3 + \frac{a_3}{\mu})\right]}$$
(4-18)

This equation describes the X-ray reflectivity from a stack of atomic layers. By measuring the specularly reflected beam at a fixed q_z value, it is possible to monitor adsorbate growth during MBE.



Figure 4-6a. Scattering of an X-ray beam from uniform atomic layers. At the anti-Bragg position, where there is destructive interference between the diffracted beams, specular beam reflectivity is extremely sensitive to surface growth.



Figure 4-6b. Scattering from an epitaxial layer of coverage θ plus scattering from the bulk. The negative sign indicates that the two beams are out of phase - the anti-Bragg position.

(a) Bragg Condition – Constructive Interference.

 $|q_z a_3| = 2\pi m$. Considering the denominator of equation (4-18),

$$\exp[-(i2\pi m + \frac{a_3}{\mu})] = \exp[-i2\pi m].\exp[-\frac{a_3}{\mu}]$$
$$= \exp[-\frac{a_3}{\mu}].[\cos(2\pi m) - i\sin(2\pi m)]$$
$$= \exp[-\frac{a_3}{\mu}].[I - 0]$$

And since $\frac{a_3}{\mu} \ll 1$, then $\exp\left[-\frac{a_3}{\mu}\right] \approx l - \frac{a_3}{\mu}$

So, substituting into ψ above,

$$\psi_{Bragg} = F(q_z) \frac{1 \cdot 0}{1 \cdot 1 \times (1 - \frac{a_3}{\mu})}$$
$$= F(q_z) \cdot \frac{1}{a_3}$$
$$\psi_{Bragg} = \frac{\mu}{a_3} F(q_z)$$
(4-19)

Since μ/a_3 is large, there is little sensitivity to surface growth at the Bragg points.

(b) Anti-Bragg Condition - Destructive Interference

 $\left|q_{z}a_{3}\right|=2\pi(m+\frac{1}{2})$ and again considering the denominator term,

$$\begin{split} \exp[-(i2\pi(m+\frac{1}{2})+\frac{a_3}{\mu}) &= \exp[-i2\pi(m+\frac{1}{2})] \cdot \exp[-\frac{a_3}{\mu}] \\ &= \exp[-\frac{a_3}{\mu}] \cdot [\cos(2\pi(m+\frac{1}{2})) - i\sin(2\pi(m+\frac{1}{2}))] \\ &= \exp[-\frac{a_3}{\mu}] \cdot [-1 - 0] \\ \psi_{AntiBragg} &= F(q_z) \frac{1 - 0}{1 - (-1) \times (1 - \frac{a_3}{\mu})} \\ &= F(q_z) \cdot \frac{1}{2 - \frac{a_3}{\mu}} \end{split}$$

Since $a_3/\mu \ll 1$ then $(2-a_3/\mu) \approx 2$ and,

$$\psi_{AntiBragg} = \frac{1}{2}F(q_z) \tag{4-20}$$

This anti-Bragg condition is equivalent to scattering from half a monolayer. The addition of an epitaxial layer with occupancy θ (0< θ <1) causes interference between the surface layer signal and the signal from the stacked layers (figure 4-6b). Under these conditions, the specular beam is extremely sensitive to surface growth.

The total scattered wave is the sum of the bulk and surface scattered waves and is given by,

$$\psi_{AntiBragg} = \frac{1}{2} F_B(\mathbf{q}) - \theta F_S(\mathbf{q})$$
(4-21)

If the adlayer and the bulk substrate are the same material then,

$$\psi_{AB} = \frac{1}{2} F(\mathbf{q}) [1 - 2\theta] \tag{4-22}$$

And since the intensity of the scattered beam is proportional to the square of the wavefunction, then,

$$I_{AB} \propto (1 - 2\theta)^2 \tag{4-23}$$

So, if the growth were perfect layer-by-layer, it would be expected that the reflected intensity would change as a function of adlayer coverage (figure 4-7a); the intensity being a series of parabolas with zero intensity when the coverage of the topmost layer is equal to half a monolayer. But, perfect layer-by-layer growth does not usually occur. More likely, growth will occur in simultaneous multilayer mode whereby the nth layer begins to grow before the (n-1)th (or even (n-2)th) layer is complete and the intensity appears as a series of damped parabola (figure 4-7b).

4.7 Photoemission Process

Irradiation of a material with electromagnetic radiation causes electrons to be emitted from the material. The energy distribution curve (EDC) of the photoelectrons consists of a smoothly decaying background due to inelastically scattered electrons, with superimposed peaks at certain kinetic energies. The positions of these peaks correspond to atomic core levels and are unique to the element being studied.

A monochromatic beam of photons is incident at an angle θ_i with respect to the surface normal and at an angle ϕ_i with respect to a crystallographic direction (figure 4-8). The photons excite electrons from the atomic core levels and these photoelectrons are emitted



Fig. 4-7a (top). Ideal layer-by-layer growth as measured at the anti-Bragg position by X-ray reflectivity. Complete destructive interference on completion of each half-monolayer and complete constructive interference at the completion of each monolayer.

monolayer. Fig. 4-7b (bottom). X-ray reflectivity of simultaneous multilayer growth measured at the anti-Bragg position.



Figure 4-8. Schematic diagram of the X-ray photemission process. The incoming beam is incident at an angle of θ_i to the surface normal and some angle ϕ_i to a crystallographic axis. The scattered beam exits at θ_e to the surface normal and at ϕ_e to the same crystallographic axis.

in a direction defined by θ_e , ϕ_e . Photoemission can only occur from those core levels with binding energies less than the incident photon energy. For metals, the convention is to define the binding energy relative to the Fermi level, E_f .

A photoelectron emitted from a core level of binding energy $E_{\rm B}$ has kinetic energy, $E_k,$ described by the relation,

$$E_k = h\nu - E_B \tag{4-24}$$

This is a simplistic approach and assumes the atomic orbitals remain in their initial configuration during photoemission (the so-called 'frozen orbital' approach) and any transition time is considered to be short ($\Delta t \sim 10^{-15}$ s). However, it is more likely that there will be some electronic redistribution which will attempt to screen the core level hole left by photoionization. The degree to which this affects the emission was considered by Koopman in 1935 [12]. The relaxation of the 'mobile' charge towards the core hole can change the kinetic energy of the emitted electron by up to several eV, resulting in shake-up satellites.

The incident photons have a penetration depth of several nanometres, but the emitted photoelectrons have a mean free path of less than 30Å, hence photoelectron spectroscopy is very surface-sensitive (figure 4-1).

Core level photoemission is characteristic for each element and this specificity is the basis of using photoelectron spectroscopy for chemical analysis. The chemical environment can be deduced from small shifts of the core level peaks – chemical shifts. Also, for many elements, a surface core level shift (SCLS) appears due to the electronic reconfiguration of the surface atoms compared to those in the bulk.

By using different experimental geometries, a variety of information can be measured. For example since the photoelectrons are scattered and diffracted by the sample, certain structural parameters, such as atomic separation, can be calculated. These values are determined using angle-resolved photoelectron spectroscopy (ARPES) whereby the photoelectron intensity distribution is measured as a function of collection angle. The large variations in the intensity of certain core level features as a function of the collection angle are used by photoelectron diffraction (PhD) to determine surface structures. Band structure (E-k) can be obtained from angle resolved photoemission from the valence band.

A semi-classical approach is used where the photon is treated classically and the emitted photoelectron is treated quantum mechanically. The photoemission intensity is dependent on the probability of exciting an electron from its initial state ψ_i to a final state ψ_f . The probability is proportional to matrix element $|M_{fi}|^2$, where $M_{fi} = \langle \psi_f | \mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A} | \psi_i \rangle$.

 $p = -i\nabla$, the momentum operator, and A is the vector potential of the incident radiation. For a monochromatic beam of photons, $\nabla_* A = 0$, so $M_{\rm fi}$ reduces to,

$$M_{fi} = \left\langle \psi_f | \mathbb{A}_{\cdot} \mathbb{p} | \psi_i \right\rangle \tag{4-25}$$

Two models are commonly used to describe the photoemission process; the one-step and three-step models.

4.7.1 One-Step Model

The whole photoemission process is considered as a single-step inelastic scattering event. The differential cross-section for the primary photoelectron emission is given by the 'golden rule' expression,

$$\frac{d\sigma}{d\Omega}(E_f,k_f^{\parallel},h\nu,\mathbb{A}) \propto \sqrt{(E_f - E_{VAC})} \sum_i \left| \left\langle \psi_f \left| \mathbf{p} \cdot \mathbb{A} + \mathbb{A} \cdot \mathbf{p} \right| \psi_i \right\rangle \right|^2 \delta(E_f - E_i - h\nu) \quad (4\text{-}26)$$

 $E_f = final state energy of the electron and <math>k_f^{\parallel}$ is its momentum parallel to the surface. ψ_f is affected by the photoemission event and takes the form of a combination of Bloch waves in the crystal which is matched across the surface to a combination of plane waves in the vacuum [13].

This model involves a lot of computational effort to calculate parameters such as the photocurrent for any particular experimental geometry, so it is usually applied to the simpler systems such as clean surfaces or very simple overlayer systems.

4.7.2 Three-Step Model

This model is less rigorous, but is easier to calculate. The photoemission process is split into 3 steps;

(a) Optical excitation of the core level electron.

(b) Transport of the electron through the solid. (This step includes the possibility of inelastic scattering by other electrons).

(c) Escape of the photoelectron through the sample surface into the vacuum.

The energy distribution curve of the photoemitted electrons $I(E,h\nu)$ may be considered as the sum of primary and secondary electrons.

$$I(E,hv) = I_P(E,hv) + I_S(E,hv)$$
(4-27)

The intensity of the primary electrons can expressed in terms that represent the three steps (a), (b) and (c).

 $I_P(E,h\nu) = P(E,h\nu).T(E).D(E)$ (4-28)

P(E,hv) is the distribution of the photoexcited electrons,T(E) is a transmission functionD(E) is an escape function.

Cardona and Ley [14] showed that both T(E) and D(E) are smoothly varying functions of E, so any structure in $I_P(E,h\nu)$ must be wholly due to $P(E,h\nu)$. $I_S(E,h\nu)$ decreases exponentially with increasing energy.

P(E,hv) is a function of the probabilities of optical excitation of electrons from occupied states, E_i , into unoccupied states, E_f .

$$P(E,h\nu) \propto \sum_{i}^{f} \int d^{3}k \left| \langle i | \mathbf{p} | f \rangle \right|^{2} \cdot \delta \Big[E_{f}(\mathbf{k}) - E_{i}(\mathbf{k}) - h\nu \Big] \cdot \delta \Big[E_{f}(k) - E \Big]$$
(4-29)

This expression includes a factor for the electron analyser as well as factors for the initial and final states and photon energy. The first δ -function ensures that the photon energy is equal to the difference in energy between the initial and final states. The second δ -function ensures that the electron energy sampled by the electron analyser is equal to the final state energy. If a constant matrix element approximation is introduced, this expression reduces to the energy distribution of the joint density of states, i.e.

$$P(E,h\nu) \propto \sum_{i}^{f} \int d^{3}k \cdot \delta \Big[E_{f}(\mathbb{k}) - E_{i}(\mathbb{k}) - h\nu \Big] \cdot \delta \Big[E_{f}(\mathbb{k}) - E \Big]$$
(4-30)

However, in metals the matrix element is not constant and the 3-step model produces a photoelectron spectrum that is a distorted copy of the energy distribution of the joint density of states. The advantage of this model is that it identifies direct transitions in E-k space making it ideal for valence band structure mapping.

4.8 Spin Polarized Photoelectron Diffraction

Spin polarised photoelectron diffraction (SPPED) is an emerging technique that can detect changes in magnetic order without the need for specialised detectors. Standard photoemission spectra are taken and any change in the sample's magnetic order is accompanied by a change in the relative intensities of the s core level multiplet peaks. Photoelectrons originating from the s core levels of atoms of magnetic metals are emitted with slightly differing kinetic energies depending on whether their spins are aligned parallel or antiparallel to the unpaired electrons of the 3d level in the case of transition metals or the 4f level of rare earths. If an emitting atom is surrounded by an array of magnetically aligned

atoms, the photoelectrons are scattered differently depending on whether they are spin-up or spin-down. The simplest form of this technique is to monitor the core *s* level as a function of temperature. In the case of rare earths, the 4*s* core level is monitored. The relative intensities of the 4s core level peaks are normalised to the high temperature (paramagnetic) limit and used to calculate a spin asymmetry term S₀ [15],

$$S_{\theta} = \left(\frac{R_{\theta}}{R_{HT}} - I\right) \times 100 \tag{4-31}$$

Where R_{θ} is the ratio of the intensities of the 4s doublet at some substrate temperature θ and R_{HT} is the intensity ratio at the high temperature limit where magnetic order has completely broken down. The temperature at which there is a loss of magnetic order is shown by an abrupt change in the relative intensities of the peaks and hence, a step change in the value of S_{θ} . The temperature at which short range magnetic order is lost can be as high as five times the Néel Temperature [16].

X-ray photoelectron diffraction (XPD) is an electron diffraction process in which an electron wave is created by the absorption of a photon and scattered by neighbouring atoms or ions and is able to selectively give ordering information on specific elements or on a specific chemical state of a given element [16]. The excitation process obeys the dipole selection rules which may, under certain conditions, be used to enhance regions of interest by using asymmetries in photoelectron emission. The primary photoelectron wave is spherical and propagates from the emitter, decaying in amplitude as 1/r. A portion of this wave will undergo scattering events with neighbouring atoms, modifying the intensity reaching the detector relative to that of an isolated emitter. Spin polarized photoelectron diffraction is a limited version of XPD, which has been shown to be well suited for studying the surface short range magnetic order in magnetic materials (though these materials include transition metals only) including antiferromagnets and may even give information on long range order. SPPED uses core level emission to get both element-specific and atomic-statespecific information. The integrated intensity under the signal of interest is monitored as the scattering potential is changed relative to the detector producing the diffraction pattern. For magnetic samples, the scattering potential can be changed by varying the sample temperature, which in turn produces magnetic fluctuations, changing the exchange part of the potential for a spin-up electron relative to that of a spin-down electron at a given scattering centre. The origin of these polarized photoelectrons is central to understanding SPPED.

The creation of a core hole by the emission of a photoelectron in a magnetic atom can leave the ion in one of two final states; that is, either with the hole parallel or antiparallel to the spin of the unpaired outer electrons, producing multiplet splitting. Emission from an outer s level is the simplest to understand since it has zero angular momentum which generally gives rise to two dominant final states. The energy separation will depend on the

relative exchange integral. As a rule, the larger the magnetic moment and the wavefunction overlap, the larger the splitting. It is this energy-resolved spin splitting that makes magnetic information possible using only an electron analyser and a source of photons, removing the need for external spin sources and spin detectors. Rare earth metals have highly localised moments so they should produce large multiplet splittings. Since the photoelectron signals are spin-resolved, the scattering from a given scatterer will depend on the relative spin orientation of the photoelectron to the spin of the scatterer. Although diffraction represents squares of sums of amplitudes and might be expected to be non-linear in the exchange term, the weak nature at the energies used leads to a dominance of first order terms and thus a linear behaviour. This suggests that SPPED has a direct dependence on the magnetic moments of the scatterers.

4.9 Circular Magnetic Dichroism in X-ray Absorption Spectra

In this work is presented circular magnetic dichroism in the $3d\rightarrow 4f$ X-ray absorption spectra of Gd deposited on Fe buffer layers, which in turn were deposited on to a Mo(110) single crystal substrate. The areas under each peak correspond to the absorption cross-sections of the 3d levels – the $3d_{5/2}$ peak at lower photon energy. When polarized light is incident on the sample, only certain transitions are allowed between the Zeeman components of the two levels concerned. This preferential absorption is shown as a difference in the lineshape between spectra collected with incident light of opposite circular polarity. The differences in the absorption cross-sections has been shown to be directly related to the orbital quantum numbers of the initial and final states involved and the ground state expectation value of the orbital angular momentum operator $\langle L_Z \rangle$ [18].

The difference in peak areas between spectra taken with left and right circularly polarized light is normalized to the unpolarized absorption spectrum with components due to photon spin parallel (μ^+), antiparallel (μ^-) and perpendicular (μ^0) to the sample magnetization. The expression used is,

$$\rho = \frac{\int d\omega (\mu^{+} - \mu^{-})}{\int d\omega (\mu^{+} + \mu^{-} + \mu^{0})}$$

$$= \frac{1}{2} \frac{c(c+I) - \ell(\ell+I) - 2}{\ell(\ell+I).(4\ell+2-n)} \langle L_{Z} \rangle$$
(4-33)

where ρ is the normalised difference in the X-ray absorption for opposite sample magnetisation. c and ℓ refer to the orbital quantum number of the initial and final states respectively, while n refers to the initial occupancy of the final state. It can be seen that the term $(4\ell + 2 - n)$ refers to the original number of holes in the final state.

It is reasonable, in the unpolarized spectrum, to assume that $\mu^0 = \frac{1}{2}(\mu^+ + \mu^-)$ which leads to,

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$$\rho = \frac{\int d\omega (\mu^{+} - \mu^{-})}{\frac{3}{2} \int d\omega (\mu^{+} + \mu^{-})}$$

$$= \frac{1}{2} \frac{c(c+1) - \ell(\ell+1) - 2}{\ell(\ell+1).(4\ell+2-n)} \langle L_Z \rangle$$
(4-34)

This expression is applied directly to the collected, normalised, absorption spectra. The integral must be taken over the whole absorption edge; that is, the total area under the spin-orbit split terms, for spectra of opposite sample magnetization. So, if $\int d\omega(\mu^+)$ $(\int d\omega(\mu^-))$ refers to the total area with photon spin parallel (antiparallel) to the sample magnetisation then equation (4-34) can be written as,

$$\rho = \frac{2}{3} \frac{\int d\omega(\mu^{+}) - \int d\omega(\mu^{-})}{\int d\omega(\mu^{+}) + \int d\omega(\mu^{-})} = \frac{1}{2} \frac{c(c+I) - \ell(\ell+I) - 2}{\ell(\ell+I).(4\ell+2-n)} \langle L_Z \rangle$$
(4-35)

Using this equation enables expectation values for the angular orbital momentum operator to be derived directly from the absorption spectra.

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Chapter 5

Spin Polarised Photoelectron Diffraction in Ultrathin Tb Films deposited on Cu(001).

- 5.1 Summary
- 5.2 Background
- 5.3 Introduction
- 5.4 Experiment
- 5.5 Results
- 5.6 Discussion

References

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5.1 Summary

This chapter is a report of the study of ultrathin Tb films deposited on to a Cu(001) substrate. Spin Polarized Photoelectron Diffraction (SPPED) was used to study short range magnetic ordering in the Tb film which was found to exist up to temperatures much higher than the bulk transition temperature. Section 5.2 explains the background to the work and previous studies using the same technique. The introduction in section 5.3 explains the principles of the experiment and why the measured parameters were chosen. Section 5.4 describes the experimental equipment with the results presented in section 5.5. The discussion in section 5.6 explains the results and relates to previous studies.

5.2 Background

First predicted in 1985 [1], Spin Polarized Photoelectron Diffraction (SPPED) is a technique that utilises the fact that the s core levels in materials can provide a source of spinpolarized electrons in a photoemission experiment. The spectra from the most loosely bound s core level states are dominated by two peaks in which the electrons are almost fully polarized in opposite directions. These electrons undergo spin-dependent scattering and diffraction during photoelectron escape from the sample. A change in the doublet intensity ratio might be expected as a function of emission direction and sample temperature due to the spin-dependent exchange scattering by the magnetically polarized valence electrons of the surrounding atoms. The data obtained for the change in intensity ratio can be used to provide information concerning the short range magnetic order in the sample.

In an antiferromagnetic system, the spin-orbit effects tend to cancel in an angleresolved diffraction measurement due to the equal numbers of emitters with up and down spin; that is, the photoelectrons detected in either member of the doublet, since the spin-orbit effect (proportional to $\underline{s}.\underline{\mathbb{L}}$) will have the opposite signs for two types of contributing emitters. Such a cancellation does not occur for the exchange interaction due to its dependence on $\underline{s}.\underline{S}$ (where \underline{S} represents the spin of the valence electrons).

Only the first few spheres of neighbouring atoms are responsible for most of the observed angular anisotropies. So the exchange-associated perturbation is expected to be sensitive only to very short range magnetic order in the specimen. The observation (or non-observation) of such SPPED effects should provide information on the presence or absence of short range magnetic order in magnetic materials above their transition temperature.

The ratio of the intensities of the core s level doublet is usually normalised to the high temperature value and plotted against sample temperature as an asymmetry factor given by [2],

$$S_{\theta} = \left(\frac{R_{\theta} - R_{HT}}{R_{HT}}\right) \times 100$$

SPPED was first observed by the same group [3] in a bulk sample of $KMnF_3$ where the specimen was observed to lose short range magnetic order at a temperature twice that of the bulk transition temperature. The ratio of the intensities of the Mn 3s doublet was monitored as a function of sample temperature and the sharpest change in the asymmetry was observed at a photoelectron emission angle of 45° , which was taken to be that the SPPED effect is dominated by the nearest neighbour Mn^{2+} ions along the [100] direction of emission. It was also found that the SPPED effects were maximised for measurements at photoelectron energies greater than 100eV.

5.3 Introduction

With the current interest in developing recording media with ever increasing storage capacity, there is a lot of interest, both scientific and industrial, in understanding the magnetic properties on the nanometre scale because as domain sizes decrease the number of atoms within the domain decreases and the magnetic properties can differ significantly from the bulk properties. There are other techniques that are used to measure the magnetic properties of rare earth and transition metals (for example circular and linear dichroism which is dealt with in chapter 7), but SPPED is notable in that it specifically measures magnetic order over the range of a few atoms. The photoelectrons emitted from an atom within the specimen are directly influenced by the emitter's nearest neighbours only and when magnetic alignment is lost, the diffraction of the photoelectrons is affected.

SPPED is based on X-ray photoelectron diffraction (XPD) which is itself well suited to surface and shallow interface studies [4]. XPD is an electron diffraction process whereby the absorption of a photon creates a photoelectron wave which is scattered by the nearest neighbours to the emitting atom as depicted in figure 5-1. The excitation process obeys the dipole selection rules which may be used to enhance regions (or directions) of interest by using asymmetries in the photoelectron emission. The primary photoelectron wave is spherical and propagates from the emitter with its amplitude decaying as an inverse function of its radial distance. The wave will undergo scattering from neighbouring atoms, modifying the intensity reaching the detector relative to that of an isolated emitter. The scattering of the photoelectron wave by any given atom will depend on the spin orientation of the photoelectron relative to the spin of the unpaired outer electrons of the scattering atom, or the unpaired electrons of the 4f shell in the case of the rare earth metals.

The creation of a core hole in a magnetic atom by the emission of a photoelectron can leave the ion in one of two final states – the hole is aligned either parallel or antiparallel



the atom will have a different energy depending the spin of the emitted photoelectron and its relation to the spins of the magnetically polarized valence electrons of the surrounding atoms. The photoelectron wave undergoes scattering from the neighbouring atoms which depends on the spin orientation of the spin of the photoelectron relative to the spins of the Figure 5-1. When a photon is absorbed and a photoelectron is emitted from the material the remaining ionised state within valence electrons of the surrounding atoms. to the spin of the unpaired electrons in the 4f shell in the rare earths producing multiplet splitting in the energy distribution curve (EDC) as shown in figure 5-2 [1].In a magnetically ordered sample, photoelectrons are emitted and diffracted slightly differently depending on whether they are spin-up or spin-down. Within the atom there is an interaction between the core level electrons and the electrons in the unfilled 4f shell resulting in multiplet splittings. Emission from a core s level is the easiest process to understand because it has zero angular momentum which gives rise to just two dominant final states. The energy separation of the doublet is dependent on the relative exchange integral – the larger the overlap between the magnetic moment and the wave function, the larger the splitting. It is this energy-resolvable spin splitting that makes the collection of magnetic information possible using only an electron analyser and an X-ray source, thus removing the need for external spin sources or spin detectors.

The relative intensities of the 4s doublet are determined by the relative spin of the photoelectron to the spins of the unpaired electrons in the 4f shell of the scattering atoms. But scattering occurs only from the nearest neighbours of the emitting atom so the spectral lineshape is dependent only on the magnetic ordering of the nearest neighbours to the emitter, thus SPPED measures the short range magnetic order that extends over a few Ångstroms and the first few nearest atoms.

Magnetic order is lost when the sample temperature is increased and bulk magnetism is lost at some critical temperature known as the Curie Temperature (T_C) in ferromagnets and the Néel Temperature (T_N) in antiferromagnets. As the critical temperature is approached from below, the spontaneous magnetization (or sublattice magnetization in antiferromagnets) drops continuously to zero. However, magnetic moments of atoms are still correlated over a few shells of nearest neighbours whilst the bulk is paramagnetic. It is this short range magnetic order that is probed by SPPED and this short range magnetic order can exist up to temperatures much higher than the bulk transition temperatures.

In SPPED experiments the chief property of interest is the intensity ratio of the spin-up to spin-down core s level photoelectron signals as a function of temperature. It might be expected from theoretical spin-spin correlation behaviour that the intensity ratio would decrease gently as the temperature is increased, but in fact there is an abrupt change observed in the spin-up photoelectron intensity relative to the spin-down intensity and this change is observed at some temperature T_{SR} , well above the bulk transition temperature. Since SPPED primarily samples nearest neighbour scattering events, the change in the scattering potential must come from the breakdown of short range magnetic order as thermal effects become more prominent and the spins of the valence electrons become randomly aligned. The spins of the neighbouring atoms move from order to disorder and the atoms are randomly aligned and this transition temperature, T_{SR} , can be between 2 and 5 times the bulk critical temperature [2].

In general, the spin polarization in each multiplet is referenced to the net valence spin (magnetic moment) of the emitter, which means that it should be possible to study both



Figure 5-2. Multiplet-split Tb 4s spectrum showing the initial and final states for an incident photon energy of hv=615eV. The predominant photoelectron spin orientations are indicated. ferromagnetic and antiferromagnetic systems which is in contrast to other electron spectroscopic probes that use external spin detectors.

It is not unreasonable to assume that the photoelectron diffraction event captures the sample in a given magnetic state because spin fluctuations have a time constant approximately 6 orders of magnitudes slower than a scattering event [5] and no spin rotation can be expected to occur in the time it takes the photoelectron to leave the emitter and scatter $(10^{-16} \text{ to } 10^{-17} \text{ seconds})$.

5.4 Experiment

Spin Polarized Photoelectron Diffraction was used to study ultrathin Tb films deposited on a Cu(001) substrate. The substrate is non-magnetic so any magnetic effects that are observed are due entirely to the adsorbate. All measurements were made under UHV and were taken using beamline 5U of the SRS at Daresbury.

The 4s core levels in rare earths are among the weakest in the electron distribution curve (EDC) with a low cross-section to UV radiation in comparison with the deeper core levels and, with the requirement that photoelectrons need to be emitted with energies of a few hundred eV, means that the 4s peaks are still on the secondary tail. So, several spectra need to be collected – a factor compromised by the rate of contamination of the rare earths. However, if the pressure is sufficiently low it is possible to obtain a satisfactory number of spectra without undue contamination of the sample. Photoemission spectra were taken of the valence region both before and after the 4s spectra were collected to check for sample contamination via the appearance of the oxygen 2s photoemission peak.

Ultrathin Tb films were deposited from a Knudsen-type vapour source on to the Cu(001) single crystal mounted on a liquid helium cooled cryostat as described in §3.6.1. The base pressure of the SURF1 chamber was 6×10^{-11} mbar and never rose above 2×10^{-10} mbar during deposition. The Cu(001) substrate was cleaned by successive cycles of argon ion bombardment and annealing, as described in §3.7 and substrate cleanliness was checked by a combination of LEED and photoemission. After deposition the sample was checked for cleanliness using photoemission to check for the presence of an O 2s peak which is indicative of oxygen contamination as low as 0.01 Langmuir [6].

The Tb 4s photoemission spectra were taken with a photon energy of 615eV with the beam incident on the sample at 45° to the surface normal. This photon energy was chosen to avoid overlap of the Tb peaks with second order features of Cu and this meant that the photoelectrons emitted from the core 4s level emerged with a kinetic energies between 200eV and 210eV. The photoelectrons were collected at specular reflectivity at 45° to the sample normal by an HA150 hemispherical analyser in the kinetic energy range 170-240eV and each data set was taken with a freshly deposited Tb film. The photon energy used is near the top end of the range for beamline 5U and is far past the influence of the harmonics. With the spectrum range extended 30eV before and after the Tb 4s peaks, there was sufficient background to ensure accurate fitting of the data. To optimise the resolution the HA150 analyser was set at 16 slits with an energy increment of 0.16eV between data points. For all scans the beam current, i_{SRS}, was noted at the beginning and end of each measurement and the spectra were subsequently normalised to a beam current of 200mA.

The samples were formed by the deposition of the adsorbate from a well outgassed Knudsen vapour source onto the cooled single crystal substrate. To minimise sample contamination, measurements at each temperature were made with freshly deposited ultrathin films, so we can be confident that the samples remained clean during the time it took to collect the photoemission spectra.

The Tb 4s photoemission spectra were collected over the range of sample temperatures 80K to 700K. Using the liquid helium cooled sample manipulator 80K was the minimum achievable and since the Néel temperature is 220K there can be no doubt that the sample was magnetically ordered. The sample was heated radiatively from two tungsten filaments set directly beneath the sample. Across the temperature range, however, the sample was measured at slightly differing pressures. At the minimum temperature, 80K, the pressure was 6×10^{-11} mbar, but rose to 9×10^{-11} mbar at the higher substrate temperatures.

5.5 Results

Photoemission spectra of the Tb 4s levels were collected for sample temperatures in the range 80K to 700K. Figure 5-3 shows several Tb 4s spectra taken at different sample temperatures. The 4s level appears as a doublet superimposed on a sloping background and when the background is subtracted the peak at the higher kinetic energy has a slightly higher intensity. As shown in figure 5-1 this high kinetic energy peak consists predominantly of photoelectrons with spins aligned antiparallel to the spins of the unpaired electrons in the Tb 4f shell. It can be seen that the relative intensities of the peaks appear to change when the substrate temperature is between 530K and 570K and this would be consistent with earlier work on MnO [2] and KMnF₃ [3] where there was a change in the intensity ratios of the Mn 3s doublet which was taken to show a transition in short range magnetic order within the crystal.

All spectra were taken across a sufficient energy range to provide the fitting program with enough background data points with which to accurately calculate a fitted background.

The spin asymmetry is calculated for each temperature and the results are plotted in figure 5-4. Although the results are a little noisy, a sharp change in the value of the spin asymmetry can be seen between 530K and 570K, which corresponds to the visual evidence of the change in the intensity ratio of the Tb 4s peaks.



Figure 5-3. Tb 4s photoemission spectra as a function of temperature showing the change in the intensity ratio at higher temperature as the short range magnetic order is lost.
For the measurements taken for Mn, as the sample temperature increases the spin asymmetry decreases slowly, but at some temperature much higher than the Néel Temperature there is a small region of temperature where the decrease is much sharper. After this sharp drop the spin asymmetry value decreases at the same negative gradient as before the transition. The temperature at which there is maximum gradient has been variously described as the temperature at which short range magnetic order is lost [1-4] and also the temperature at which magnetic order in the surface is lost [8]. The photoelectrons are collected at kinetic energies of approximately 200eV which means that the measurements are surface sensitive so it not unreasonable that the transition may be due to changes in the magnetic ordering at the surface.

The Tb 4s spectra were analysed using an in-house program which fits a Doniach-Sunjic lineshape [7] to the raw data of the photoemisson spectra. When each Tb 4s photoemission spectra was collected, the SRS beam current was noted and all the spectra were subsequently normalised to a beam current of 200mA, though this was not strictly necessary since only the intensity ratio of the doublet was of interest. The analysis program fits the background with a polynomial of a given order and also gives the option of convoluting the Doniach-Sunjic lineshape with a Gaussian to mimic the resolution of the instrumentation. The analysis program prompts for the input of peak positions, peak heights and peak widths which are used as a starting point for the fitting procedure, before returning values for these parameters which produce the lowest χ^2 value. A fitted spectrum for the sample held at 80K is shown in figure 5-5 where the two fitted peaks are shown with the background subtracted and the fitted lineshape is superimposed over the data points.

The lineshapes of the photoemission spectra are determined by two factors; the lifetime of the core hole which is Lorentzian and the resolution of the instrumentation which is Gaussian. The results obtained from the fitting procedure were used to calculate the spin asymmetry as a function of substrate temperature. For each temperature θ the ratio of the intensities of the fitted peaks R_{θ} was normalised to the intensity ratio at the high temperature limit R_{HT} and a value for the spin asymmetry was obtained from the formula given in §5.1,

$$S_{\theta} = \left(\frac{R_{\theta}}{R_{HT}} - 1\right) \times 100$$

 R_{θ} is the ratio of the integrated areas of the Tb 4s doublet at temperature θ and is normalised to the high temperature value, R_{HT} at which we can be confidant that there is no magnetic order in the sample because thermal energy will have broken up even the smallest regions of magnetic order.



Figure 5-4. Spin asymmetry plotted as a function of sample temperature. Note the loss of asymmetry at approximately 560K which is attributed to the loss of short range magnetic order. The Néel temperature of Tb (230K) is represented by the dashed line as is the temperature at which short range magnetic order is lost.

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5.6 Discussion

It is known that the Néel Temperatures and Curie Temperatures of magnetic materials can be significantly higher for the surface than the bulk values, prompting the idea that magnetic order can exist within the surface long after it has been lost in the bulk. A recent Monte Carlo calculation [8] used this premise to suggest that the step change in the value of the spin asymmetry is in fact a transition in the surface magnetic order.

This may indeed be the case, but with such a thin film none of the atoms within the film could be considered as truly bulk atoms. Zhang *et al* [8] considered nearest neighbour and next-nearest neighbour interactions and found that the nearest neighbour interactions were by far the most significant. The loss of short range magnetic order was entirely due to loss of magnetic alignment with an atom's nearest neighbours in-plane and in the planes above and below and it was suggested that the effect was contained entirely within the surface.

From the work presented here there is no significant contribution from surface or interface atoms, but a small contribution from both. Since the Tb 4s peaks are very weak, high statistics are required for each photoemission spectrum which means that multiple spectra were taken and, due to the finite data collection time to avoid sample contamination, the noise level is still quite high, but still when the peaks were fitted with a single contribution each there was evidence of a sharp change in the spin asymmetry at high temperature. This can be taken to be a loss of short range magnetic order in the film.

However if the temperature-enhanced magnetic order were due to atoms in a specific environment then it would be expected that spin asymmetries calculated from those fits where there were two and three contributions would show a step when plotted as a function of temperature. When the spin asymmetries were calculated separately just from those contributions attributed to surface and interface atoms there was no change in value at any temperature. But since there is a change when calculated from the single contribution, it seems that there must be changes in the surface and interface asymmetries but they do not show above the noise level.

Another implication to be drawn is that short range magnetic order exists up to high temperature regardless of the environment of the contributing atoms. The films studied here were 6ML thick, but there was no evidence that the short range magnetic order was confined to either the surface atoms or interface atoms alone.

Considering simply the peak intensities in the Tb 4s doublet, each peak was fitted with a single contribution to obtain values for the intensities of the individual peaks. It was found that there was a step-like change in the value of the spin asymmetry ratio at a temperature between 530K and 570K at which we can assume that there is a loss of short range magnetic order. The Néel Temperature of Tb is 230K so the transition occurs at 2.4T_N which compares with the proposition of Fadley and co-workers [1-4] that short range magnetic order is lost at some temperature between 2T_N and 5T_N.

The Tb film was calibrated by RBS to be 6ML thick so it might be expected that there should be contributions from atoms in different environments, that is surface, bulk and interface atoms. So, the Tb 4s doublet was fitted using both two and three contributions – two contributions being from surface and interface atoms and the three contributions being from surface atoms.

In the case of the double- and triple-contribution fits, each of the contributions to each peak in the doublet can be assigned as surface, bulk or interface contributions. Considering either of the peaks in the doublet fitted with three contributions, the contribution with the highest kinetic energy value is from the surface atoms. The contribution with the next highest kinetic energy is from the interface atoms and the third is from the bulk atoms.

Since the single-contribution fit is simply the sum of the double-contribution, it was expected that there should be a change in the asymmetry value at $550(\pm 20)$ K for one or more of the surface, bulk or interface cases. No such step was observed above the noise for any of the surface asymmetry, bulk asymmetry or interface asymmetry. However, if there are small steps indistinguishable above the noise, then the sum of these individual steps is visible as the change in value of the asymmetry value in the single-contribution fits.

So, the conclusion must be that the loss of short range magnetic order is throughout the whole film and not limited to just the surface atoms.

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Chapter 6

The Growth of Gd Ultrathin Films on Mo(110) studied using Surface X-Ray Diffraction.

- 6.1 Summary
- 6.2 Introduction
- 6.3 Experiment
- 6.4 Curve Fitting
- 6.5 Gd Growth As A Function Of Substrate Temperature
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 - 6.7.1 Background
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- 6.8 Conclusion

References

6.1 Summary

In this chapter measurements are described for the growth of ultrathin Gd films on the Mo(110) substrate and how the growth mode is affected by changes of substrate temperature and the presence of oxygen.

Section 6.2 provides an introduction with a brief summary of the theory behind surface X-ray diffraction which is treated in more detail in §4.5 and §4.6. The experimental arrangement is described in section 6.3 followed by an explanation of the curve fitting procedures used in the analysis programs in section 6.4.

The results of the growth at room temperature presented in section 6.5 and a brief treatment of the variation of growth mode as a function of substrate temperature is carried out in section 6.6. Section 6.7 deals with the oxygen-mediated growth of Gd films. A brief introduction to other studies that have looked at the use of surfactants is followed by the results obtained from dosing the Mo(110) crystal surface with oxygen prior to deposition of the Gd film.

6.2 Introduction

Ultrathin magnetic films and multilayers, produced by epitaxial growth, exhibit a wide variety of magnetic properties which depend on the deposition conditions and substrate choice. The rare earth elements are of particular interest because they are characterised by highly localised and partially filled 4f orbitals. The magnetic interactions are of the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) type, which implies that not only are many magnetic phases expected, but that particular control over the growth conditions is required to ensure that specific atomic arrangements are produced.

Gadolinium on molybdenum is an attractive system for study since Gd orders ferromagnetically below 293K whereas Mo is paramagnetic at all temperatures. They do not form any known alloys and have very low mutual miscibility. Little is known of the magnetic properties of Gd on Mo, but measurements using the similar W substrate show conflicting results. Farle *et al* [1] report that for a 5 monolayer film deposited at room temperature and then annealed, the Curie temperature (T_C) is reduced by 50% compared to the bulk. This is in contrast to earlier measurements for films deposited at 720K which showed only a small change of T_C [2]. Heys *et al* [3] have reported a giant magnetic moment for sputtered Gd/W superlattices, in contrast to earlier measurements and theoretical predictions [4]. Such disagreements can be attributed to differences in the microstructure of the films and the presence of defects and strain fields.

X-ray diffraction is now well established as a powerful tool for the study of surfaces and overlayer structures and has been extended to the determination of growth [5]. This chapter reports a study of the growth of Gd on the Mo(110) surface using X-ray

scattering which confirms that the structure of the films is critically dependent on the ambient conditions such as the substrate temperature and, in particular, the exposure to contaminants such as oxygen.

6.3 Experiment

All the measurements were made on beamline 9.4 at the Daresbury Synchrotron Radiation Source using the 6-circle surface X-ray diffractometer [6, 7]. X-rays of wavelength 0.9Å from the 5 Tesla wiggler were selected using a Si(111) monochromator [8]. The scattered X-ray intensity was recorded with a cooled germanium detector mounted behind two sets of four-jaw slits to define the angular resolution.

The sample was mounted inside the LUXC ultra high vacuum chamber which has been described already in §3.5. The chamber was equipped with an electron energy analyser for measuring Auger electron spectroscopy (AES), a low energy electron diffraction (LEED) optics and metal vapour sources. As stated previously, the configuration of the chamber allowed simultaneous recording of the reflected X-ray and Auger electron signals during deposition onto the sample surface. The base pressure of the chamber was 8×10^{-11} mbar and no detectable pressure rise was observed during deposition.

Figure 6.1 shows the variation in intensity of the reflected X-ray signal as a function of the angle of incidence of the X-rays. Figure 6-1a was measured from a clean Mo substrate and figure 6-1b from a thick Gd film. The peaks are due to constructive interference of reflected beams from adjacent layers. For adjacent Mo layers there is constructive interference for an incident angle of 6° , but for Gd layers the incident angle is 9° . As explained in §4.6 X-ray diffraction is most sensitive to surface growth at the anti-Bragg position of destructive interference. Thus the specularly reflected X-ray signal was recorded at an incident angle of 4.5° which corresponds to the reciprocal lattice vector (0.39, 0.39, 0) of the body centred cubic structure of Mo. With this geometry, scattered waves from adjacent (0001) planes of the bulk, hexagonal close-packed structure (separated by 2.891Å) are out of phase.

6.4 Curve Fitting

The growth curves are fitted using a theoretical model for bilayer growth [9] and the variation of several parameters allows the best fits to be achieved. Initially the curves are fitted for the first oscillation which corresponds to the first monolayer. This is achieved by varying such parameters as deposition rate (R), the coverage (θ) and the height of the first Gd layer (d₁). The height of the second layer (d₂) is, of course, set to zero for fitting the first



Figure 6-1. Variation of the reflected X-ray intensity as a function of incidence angle θ for clean Mo(110) (above) and deposited Gd (below).

monolayer. The second oscillation is fitted using the results of the first layer and allowing d_2 to vary.

If the growth was perfectly layer-by-layer, the X-ray intensity would oscillate as a series of parabolas due to the surface and bulk signals being successively in and out of phase as the adlayers grow. The values returned by the fitting procedure compare very well with the classical values for atomic diameters as shown in Table 6-1.

	Gd	Mo
Crystal structure	hcp	bcc
lattice parameter, a (Å)	3.63	3.15
lattice parameter, c (Å)	5.78	
Nearest neighbour distance, nnd (Å)	3.58	2.72
Density (gcm ⁻³ , or 10^3 kgm ⁻³)	7.89	10.22
Concentration $(10^{22} \text{ cm}^{-3}, \text{ or } 10^{28} \text{ m}^{-3})$	3.02	6.42
Standard atomic diameter in a	3.60	2.80
12-coordinated metal (Å).		

Table 6-1. The data presented here are at room temperature and atmospheric pressure for the most common form of the elements.

6.5 Gd Growth as a Function of Substrate Temperature

The deposition of Gd was carried out with the substrate held at several different temperatures and the change in growth mode can be seen quite clearly in figure 6-2 where each growth curve was measured at the Gd anti-Bragg position of α =9°. The low temperature growths (T<300°C) share similar features. The intensity falls rapidly at the onset of deposition, dropping to about 10% of the initial value before rising to a sharp peak. This point is taken to be the completion of the first monolayer and the intensity is about 40% of the initial intensity measured from the clean substrate. During growth of the second monolayer the intensity drops to another minimum before rising to a second peak and this is where the spectra begin to differ.

For the room temperature growth, the second peak is much lower in intensity than the first followed by a third, slightly higher, peak. Further deposition shows no features in the growth curve which indicates rough growth.



Figure 6-2. Variation of the growth curves for clean Gd on Mo(110) as a function of substrate temperature.

At 120°C the second peak is broad, but with a shoulder on the leading edge. After the second peak there are again no features in the X-ray signal indicating rough growth.

At 255°C the second peak is as pronounced as the first peak, but slightly wider and higher in intensity. This peak is followed by a second minimum and oscillations are quite clearly visible as deposition time increases. This is a surprise because the tendency is for the growth to become increasingly rougher as the substrate temperature is increased. However checking the Auger spectra for this deposition does show a minute trace of oxygen at 510eV and the carbon Auger peak at 272eV is prominent. This may be enough to induce some degree of layer-by-layer growth though not as dramatic as when the substrate was later deliberately dosed with oxygen gas.

Note, however, that at the higher temperatures $(T>350^{\circ}C)$ the growth curves are much different to the lower temperature growths. These growth curves follow the same general pattern; a sharp dip in the intensity at the onset of deposition down to a minimum before rising to a plateau after which there are no further features. The value of the intensity at this plateau is roughly that of the first peak intensities in the growths at lower temperatures implying the completion of a monolayer. Since the signal remains at a constant intensity during further deposition, the Gd must be growing as islands. The initial dip and rise in intensity indicates the growth of a monolayer before islanding occurs; that is, Stranski-Krastanov growth.

6.6 Growth of Gd Films at Room Temperature.

Clean Gd films were grown on the Mo(110) single crystal to study the growth mode and compare with the previous growth study [10] that was confined to LEED/Auger techniques.

The growth curve measured at room temperature is shown in figure 6-3. The X-ray intensity decreases sharply at the onset of deposition and rises to a sharp peak after approximately 600s. After the second minimum there are two peaks much smaller in intensity than the first before the X-ray signal becomes flat and featureless.

Fitting these growth curves is difficult because the analysis program tries to fit a parabola to the growth curve, but the oscillation is not perfectly parabolic. Although the fitting procedure does produce fits which can look significantly different, the parameters obtained from these fits are surprisingly similar. Also, with the second peak being much lower in intensity than the first, no meaningful values could be obtained for the separation between the first and second monolayers.



at room temperature. The inset shows an AES spectrum collected at 60min. into the deposition. Note that there is no oxygen peak at 510eV. Figure 6-3. Growth curve of clean Gd on Mo(110) recorded at the Gd anti-Bragg position of α =9. and grown

6.6.1 Results

X-ray intensity curves were recorded for the growth of clean Gd on clean Mo(110). In §4.6 it was shown that there is greatest sensitivity to growth when the reflected X-ray intensity is measured at the point of destructive interference for the adlayer. The position for destructive interference is called the anti-Bragg position. In the case of Gd adlayers, the highest sensitivity is obtained at $20=9^{\circ}$ (an incident angle of $4\cdot5^{\circ}$) and it was at this angle that most of the growth curves were measured. For comparison, the X-ray signal was also recorded at the Mo anti-Bragg position of $20=12^{\circ}$ (an incident angle of 6°). The curves were fitted with a parabolic fitting routine and the results obtained for the separation of the first Gd layer from the substrate were consistent within the errors calculated.

The curves are not perfectly parabolic, but can be fitted to a good approximation though the fitted parabolas peak at an intensity that is higher than the measured peak. There is a rounding off of the peak because the growth is not perfectly layer-by-layer and the second layer is beginning to form just as the first is completed.

All the growth curves return values for d_1 and d_2 that are consistent with each other. The curves are fitted to the first intensity maximum varying the parameters d_1 , d_2 , deposition rate and monolayer coverage in order to obtain the best fit.

The classical radii for Mo and Gd are 1.4Å and 1.8Å respectively and if the atoms are treated as hard spheres, a Gd atom sitting on top of a Mo atom gives an interlayer separation of 3.2Å. The maximum separation for the second layer, d₂, would be if the Gd atoms sat directly on top of the atoms in the layer below, that is $d_2 = d_1 + R_{Gd} + R_{Gd} = 3.2+1.8+1.8 = 6.8Å$.

In the theory for the oscillations in the case when the growth is perfect layer-bylayer, the minima should be at zero intensity for homogeneous adlayers. As for heterogeneous epitaxy, the first minimum need not necessarily be zero because the interference is between waves scattered by different elements, but subsequent minima ought to approach zero because the interference from the top but one layer is from waves scattered by atoms of the same element as in the top layer.

Figure 6-3 shows the variation of the reflected X-ray intensity as a function of deposition time for the growth of clean Gd on the clean Mo(110) surface measured at $2\theta = 9^{\circ}$. At the onset of deposition the X-ray intensity drops sharply to a minimum after approximately 7min. before rising to a sharp peak at 12min. The intensity falls sharply again to almost zero intensity before rising to a second peak with approximately $\frac{1}{5}$ the intensity of the first peak. A third peak follows with slightly higher intensity than the second before the

Figure 6-4 shows the first two oscillations of this growth curve together with the results of the fitting procedure. The calculated curve is shown as a dashed line. The first

X-ray signal becomes constant with no features.



shown with the fitted curve superimposed. The first oscillation is modelled well, but the fitting routine pulls away from the data for the second because the growth is not ideal layer-by-layer. The interlayer spacing between the substrate and the first monolayer is calculated to be $3.12(\pm 0.02)$ Å.

oscillation is modelled well but the fitting routine pulls away from the recorded data in the second oscillation and no meaningful results were obtained for the second interlayer spacing.

For this growth recorded at the Gd anti-Bragg position, $2\theta = 9^{\circ}$. The curve fitting procedure returns a value of $3 \cdot 12(\pm 0.02)$ Å with a reduced χ^2 value of $2 \cdot 4$. The standard procedure to calculate the error is to change the value of d₁, the first interlayer spacing, until the value of the reduced χ^2 increases to its minimum value +1. The calculated coverage of the first monolayer was calculated to be $\theta = 0.76$ where $\theta = 1 \cdot 0$ corresponds to the unrelaxed Mo(110) plane.

Figure 6-5 shows a second growth curve measured during the deposition of a Gd film, but this time measured at the Mo anti-Bragg position of $2\theta = 12^{\circ}$. The rate of deposition is slightly faster in this case but the relative positions of the peaks and troughs are consistent. The intensity drops sharply at the onset of deposition to a minimum after 5min. before rising to the first peak at 10min. Note that in this case the intensity of the peak is higher than the initial background level before deposition. If the growth were regular layer-by-layer then it might be expected that there would be a second minimum after 15min. This is not the case, but there is a shoulder on the trailing side of the peak at precisely this time and the second minimum is eventually reached after approximately 25min. After the second minimum the reflected X-ray intensity rises slightly to an intensity that is retained for the remainder of the deposition.

The fitted curve for this deposition is shown in figure 6-6. The first oscillation only is fitted since the second oscillation is complicated by the appearance of a shoulder which disrupts the fitting procedure and meaningless results for the interlayer spacing are returned. The analysis program returned a value of $d_1=3\cdot15(\pm0\cdot2)$ Å with a monolayer coverage of $\theta = 0.78$ when fitting the first oscillation. This is consistent with the results obtained for the growth curve recorded at $2\theta = 9^{\circ}$ and is close to the maximum of 3.20Å obtained if the atoms are considered as hard spheres sitting on top of one another.

6.7 Oxygen-modified Growth of Gd Films

6.7.1 Background

The growth of thin films on metallic substrates is determined by both lattice strain and the surface free energies of the adsorbate and substrate. The fundamental growth modes are layer-by-layer (Frank-van der Merwe), islanding (Volmer-Weber), one or more layers followed by islanding (Stranski-Krastanov) and simultaneous multilayers [11].

The epitaxial growth of adlayers is a balance between kinetics and energetics and, traditionally, the inhibition of islanding in the growth of heteroepitaxial films was attempted by restricting the growth kinetics. There were two methods that were usually used; decreasing the growth temperature or increasing the growth rate. However, restricting the





Figure 6-6. The first oscillation is fitted for the growth curve as measured at the Mo anti-Bragg position of 20=12°. The curve is parabolic only up to the first peak which precludes modelling the growth past this point. The interlayer separation between the substrate and the first Gd monolayer was calculated as $3.15(\pm0.02)$ Å. growth kinetics also restricts the epitaxy of the film. Another option is to alter the energetics of the growth via the use of a surfactant whereby both island formation and interdiffusion are inhibited without the sacrifice of epitaxy [12-21]. The requirements for a surfactant are that it reduces the surface free energies of substrate and adsorbate and that it is sufficiently mobile to avoid incorporation into the adlayers.

Vrijmoeth *et al* [20, 21] have studied the homoepitaxial growth of Ag on Ag(111) using Sb as a surfactant. The role of Sb in the promotion of layer-by-layer growth has been monitored using surface X-ray diffraction (SXRD) and scanning tunnelling microscopy (STM). With no surfactant present, no layer-by-layer growth is observed over the temperature range 175-575K and the growth gradually changes from step flow to multilayer growth with several layers simultaneously exposed. However, after dosing the substrate with 0.2ML of Sb layer-by-layer growth was observed. From the STM studies it was proposed that there were two origins to the change in overlayer growth;

(a) Sb slows down the adatom mobility both on the substrate and on top of the growing islands. The increased surface diffusion barrier directly affects the additional energy barrier at the step edge and induces the smooth growth.

(b) Sb slows down the adatom mobility along the step edges. This gives rise to irregular, dendritic, island shapes and induces a further enhancement of the interlayer transport. It was found that heterogeneous nucleation is important only in the first layer and is not responsible for the observed continuous oscillations.

From the STM studies, it was seen that up to 17 layers remained open during growth in the absence of the surfactant material, but after deposition of Sb only the uppermost three layers remained open and uncoalesced.

It was encouraging that early depositions of Gd on Mo(110), made before the evaporant was fully outgassed, showed the oscillations in X-ray intensity to persist longer than in subsequent depositions when the Gd was clean. An example of the growth curves for the deposition of dirty Gd is shown in figure 6-7. These oscillations were regularly spaced though the peak intensities decayed slowly during the deposition. The Auger spectrum is shown in the inset and was collected 90min into the deposition. As is usual when a rare earth adsorbate is not sufficiently outgassed, the main contaminants are carbon and oxygen as shown by the C KLL peak at 272eV and the O KLL peak at 510eV. These oscillations vanished during subsequent depositions when the vapour sources were properly outgassed and the Gd was clean and AES spectra taken during later depositions of clean Gd showed a small carbon peak, but no oxygen peak implying that it was the presence of oxygen promoting layer-by-layer growth. Since high purity oxygen gas is used in the cleaning procedure of Mo, a promising surfactant material was conveniently available.

It will be shown here that the epitaxial growth of clean Gd was greatly improved when the Mo(110) substrate is exposed to a controlled dosage of oxygen before deposition of the Gd films. Early depositions of Gd, made when the evaporant material was



contaminant being oxygen as shown in the Auger spectrum (inset) by the presence of the KLL line at 510eV. Note the regularity of the peaks implying layerwise growth and the decay in intensity indicating simultaneous multilayer growth.

insufficiently outgassed, did show oscillations in the reflected X-ray intensity and the indications were that layer-by-layer growth was occurring to some degree.

6.7.2 Results

Before deposition the clean Mo(110) surface was exposed to a controlled dosage of pure oxygen gas. Oxygen was admitted into the UHV chamber up to a partial pressure of 10^{-8} mbar for 25s; an exposure of 0.25 Langmuir. After this exposure, the chamber vacuum was allowed to recover to its base pressure (1x10⁻¹⁰ mbar) before beginning the Gd deposition.

The growth curve measured at $\alpha = 9^\circ$, the Gd antiBragg position, is shown in figure 6-8 for the growth of Gd on the Mo(110) surface that has been pre-dosed with 0.25L of oxygen. Oscillations are present up to 7 monolayers, though beam loss after 4500s meant that further oscillations could not be observed. The peaks in the X-ray intensity are regularly spaced at 650s implying a uniform rate of deposition during the growth, and the periodicity is consistent with the earlier AS-t work of Nicklin [10]. The first peak at 650s corresponds to the break in linearity of the AS-t curve that was recorded simultaneously with the growth curve. A qualitative mechanism for the surfactant mediated growth can be proposed from the shape of the growth curve. At the onset of deposition the intensity drops to a non-zero minimum which is about $\frac{1}{6}$ the value of the initial intensity at t = 0, defined here as I(0). The intensity rises until, at the completion of a monolayer, the intensity reaches a maximum of $\frac{1}{2}$ I(0). The intensity falls to a second minimum of almost zero intensity before rising to its second maximum. The second and third maxima are approximately $\frac{1}{3}I(0)$ so that it appears that the growth is slightly rougher in the second and third monolayers than in the first. However, there is an unexpected drop in the intensities of the maxima from the fourth monolayer upwards. Although the minima are consistently close to zero (the count rate is ~50 s⁻¹ at the minima) the maxima are down to about $\frac{1}{6}$ I(0). According to the theory, the reduced intensity is an indication of increased roughness in the top layer of the adsorbed film, but if this is the case then the roughness increases suddenly at the onset of the fourth monolayer, but doesn't increase thereafter.

Auger spectra taken during the deposition show that the intensity of the oxygen KLL line at 510eV decreases during deposition so we can be sure that the oxygen remains at the substrate surface and is buried by the Gd layers. It is proposed that oxide clusters form at the Mo(110) surface which results in lattice parameters in this monolayer that are different to the values of bulk Gd and different also to when Gd is deposited directly onto the clean Mo(110) surface. If the monolayer is relaxed and interlayer transport is improved in the presence of the oxide clusters then subsequent deposition ought to tend towards good epitaxial growth until the oxide clusters have been buried. After a coverage of 3 monolayers it is not unreasonable to suppose that any structures at the interface will have minimal effect on the newly deposited atoms and the atomic arrangement in subsequent layers will tend



Figure 6-8. The growth curve of clean Gd on Mo(110) after dosing the surface wih 0.25L of oxygen. Inset (a) is an Auger spectrum taken soon after beginning deposition showing Mo, C KLL (272eV) and O KLL (510eV) peaks. Inset (b) was taken after 60min of deposition and the oxygen peak has disappeared, implying that the oxygen has been buried.

towards the bulk structure which introduces strain into the overlayer and the growth becomes rougher. This will reduce the reflected intensity which is what is observed for the coverage of 4 monolayer and thicker.

The shape of the growth curve is much more similar to that of ideal growth as shown in figure 4-7 and reasonable results are obtained for the interlayer separation of the first and second adlayers. The first two oscillations have been modelled and the result is shown in figure 6-9. The first oscillation is not perfectly parabolic, but the overall curve is fitted well.

The values obtained from the fitting procedure were $d_1 = 3 \cdot 17(\pm 0 \cdot 02)$ Å and $d_2 = 6 \cdot 40(\pm 0 \cdot 02)$ Å. The value for d₁ is close to the maximum value expected when considering the atoms as hard spheres stacking on top of each other. The value for the coverage of the first layer was returned as $\theta = 0.68$ which shows that the monolayer has a higher lattice constant than the case where deposition was onto the clean surface. These values differ from those previously published [22] due to an error in the analysis program that has since been corrected.

Another problem to be solved for the growth mechanism is the role of oxygen in promoting layer-by-layer growth. The work by van der Vegt et al in the studies of homoepitaxial growth of Ag on Ag(111) showed that the Sb atoms 'floated' through the adlayers as Ag was deposited. The fact that the oscillations decay over a period of about 20 monolayers implies that only a fraction of the Sb atoms migrate from one layer into the next, newly deposited, layer. When oscillations had ceased the introduction of more Sb restarted layer-by-layer growth. The role of the oxygen is slightly different in the growth of Gd on Mo(110). Auger electron spectra taken during the deposition showed that a rapidly decreasing oxygen peak indicating that the oxygen was being buried at the interface and not segregating through the adlayers. Although the oxygen is buried, there is still layer-by-layer growth probably due to the fact that there is a much improved registry between the first and second monolayers. With no oxygen, the Gd forms a densely packed hexagonal structure that is 5% contracted with respect to the bulk (0001) plane. This introduces strain into subsequent layers so there should be no surprise that islanding and rough growth occurs. Layer-by-layer growth in heterogeneous systems usually occurs when the substrate and adsorbate have similar lattice parameters. It is proposed that the role of oxygen in the growth of Gd is to act as a nucleation site. Gd is easily oxidised and it is probable that Gd atoms cluster about adsorbed oxygen atoms where the lattice parameters in the first monolayer are enlarged and approximate more to the bulk values. This means that there will be less strain in subsequent layers and layer-by-layer growth should be more energetically favourable. Unlike Sb in the growth of Ag on Ag(111), the reintroduction of oxygen does not restart the layer-by-layer growth of Gd, which implies an interface effect.

The growth curve of clean Gd on clean Mo(110) shows one peak followed by two, equally spaced, weaker peaks. This is in agreement with the earlier LEED and AES studies [10] which showed rough growth after the completion of one monolayer. However, there is



Figure 6-9. The oxygen-mediated growth curve is modelled up to the second oscillation. The fitting routine models the curve well though it does pull away a little from the data at the cusp of the first peak. The values returned from the fitting procedure were $d_1=3.17(\pm0.02)$ Å and $d_2=6.40(\pm0.02)$ Å. So, the interlayer separation between the first and second Gd monolayers is $3.23(\pm0.04)$ Å. a dramatic change in the growth mode of the Gd adlayers when, prior to deposition, the clean Mo surface was exposed to 0.25 Langmuir of oxygen. Oscillations with regularly spaced peaks are clearly present to beyond 6 monolayers which is evidence for improved layer-by-layer growth. This improvement implies that there is an increased inter-layer mass transport and hence, a reduced tendency to form multilayer structures. Others [19, 20] have shown that the presence of impurities can greatly affect the growth kinetics of adsorbates. In both cases it is Sb that promotes layer-by-layer growth for Ag deposited on Ag(111).

6.8 Conclusion

The growth of Gd films has been studied under a variety of ambient conditions and it has been shown that the growth mode can vary dramatically.

The growth of Gd films as a function of substrate temperature shows a general trend towards Stranski-Krastanov growth as the substrate temperature is increased. Below 350°C the completion of the first monolayer is followed by growth where subsequent layers begin before the completion of the previous one. This is manifested in the reflected X-ray intensity as smaller peaks after the large, sharp peak which signifies the completion of the first monolayer. However, above 350°C the growth curves follow a similar pattern. The reflected X-ray intensity drops to a minimum before rising to a region of constant intensity which persists for the remainder of the deposition. This is consistent with the formation of a monolayer followed by island formation, that is Stranski-Krastanov growth.

The growth mode of clean Gd films at room temperature agrees very well with earlier work [23] in that there is the formation of the first few monolayers before the growth becomes progressively rougher. The first monolayer appears to be completed before the second monolayer starts, but above this the layers begin to form before the completion of the previous layer.

With the introduction of oxygen before deposition of Gd, the epitaxial growth of the Gd film is much improved with oscillations in the reflected X-ray intensity extending up to 7 monolayers. It is proposed that the oxygen forms oxide clusters on the Mo(110) surface which act as nucleation sites for Gd metal growth. The nucleation of many islands implies a high step density and therefore a greater chance on incoming Gd atoms moving to the lower level to maintain the development of two-dimensional structures. This is a similar model to that proposed by Dastoor [13] for the homoepitaxial growth of Cu on Cu(111) in the presence of oxygen. The precise mechanism whereby the oxide complexes, buried at the interface, continue to influence the growth of successive Gd layers is not clear. It is possible that completely relaxed layers are quickly formed with dislocations localised in the vicinity of the nucleation sites.

So, epitaxial growth of the Gd film can be greatly improved by the introduction of a trace amount of oxygen onto the Mo(110) crystal. It would be of interest to compare this with the growth of other rare earth metals, possibly on different substrates.

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Chapter 7

Circular Magnetic X-Ray Dichroism in Gd Thin Films

- 7.1 Summary
- 7.2 Introduction
- 7.3 3d XAS in rare earth metals
- 7.4 Magnetic Dichroism in X-ray Absorption Spectra
- 7.5 Experimental Arrangement
- 7.6 Gd Film Preparation
- 7.7 Results
- 7.8 Ground State Expectation Value of the Orbital Angular Momentum.
- 7.9 Discussion

References

7.1 Summary

This chapter reports a Circular Magnetic X-ray Dichroism (CMXD) study of Gd films. The introduction of section 7.2 summarises the short history of Circular Magnetic X-ray Dichroism and explains why the technique is particularly well suited to rare earth metals. Section 7.3 deals specifically with X-ray absorption in the rare earth metals with the emphasis on Gd while section 7.4 presents the sum rules that relate the X-ray absorption spectra to the expectation values of quantum momenta.

Section 7.5 describes the experimental arrangement with a brief description of the sample heater designed and built specifically for this experiment. Section 7.6 presents Secondary Electron Emission Crystal Current measurements taken during the growths of various Gd films with emphasis on the difference in the lineshape depending on whether the Gd is deposited directly onto the Mo(110) crystal or onto the Fe buffer layer.

The CMXD results are presented in section 7.7 and they are related to the expectation value of the orbital angular momentum in section 7.8. Section 7.9 is a summary of the results obtained.

7.2 Introduction

Magnetic dichroism is generally defined as the difference in the absorption rate of differently polarized incident light by a magnetic sample. In particular, circular magnetic dichroism is measured as the difference in the absorption of left- and right-circularly polarized light. At the microscopic level the absorption rates will differ only if there is simultaneous occurrence of electron relativistic interaction (predominantly electron spin-orbit coupling) and spin-polarization (that is, magnetization).

Ultrathin metallic films produced by epitaxial growth exhibit a rich variety of magnetic properties which can depend on substrate choice and ambient conditions during the deposition. The rare earth elements in particular are characterised by highly localised, partially filled 4f orbitals. The magnetic interactions are of the Ruderman-Kittel-Kasuya-Yosida (RKKY) type implying that many magnetic phases may be possible and the growth conditions can dramatically affect the magnetic properties. Film thickness can have a major effect on a metal's magnetic properties. For example, the Curie temperature of Gd decreases dramatically as the film thickness decreases below a few monolayers [1]. The Curie temperature of Gd is 293K and room temperature measurements of magnetism are severely compromised. However, if an ultrathin layer of a magnetic material is deposited on to the substrate prior to deposition then magnetism can be induced in a Gd film deposited on top of the magnetic material.

Circular magnetic X-ray dichroism (CMXD) was first predicted in 1985 to be observable in the $M_{4,5}$ X-ray absorption spectra of rare earth elements [2] and was followed by the first experimental proof in 1986 by van der Laan *et al* [3] when strong X-ray dichroism was shown in the $M_{4,5}$ absorption edge structure of rare earth metal compounds. The first experiments to measure magnetic X-ray dichroism in ultrathin rare earth overlayers were made by Goedkoop *et al* [4]. Tb films were deposited on a Ni(110) substrate and the effects were shown to strongly dependent on interface morphology showing the potential of CMXD to be a powerful tool with which to study magnetic and crystal field interactions at surfaces and interfaces.

The background for the measurements can be described in an atomic-like model for the rare earth $M_{4,5}$ absorption. In these spectra, a 3d electron is excited into the partially empty 4f shells and a complicated multiplet structure is observed corresponding to the $3d^94f^{n+1}$ final state multiplet. These multiplet structures have been simulated very accurately with atomic multiplet calculations [5].

There is much interest in the magnetic properties of ultrathin metal films and the rare earths in general. To understand effects such as interlayer exchange splitting and magneto-resistance, a knowledge of the orbital and spin components of the magnetic moments is desirable. One of the most popular, and successful, methods of separating spin and orbital magnetic moments is circular dichroism in X-ray absorption spectroscopy (XAS), which utilises the integrated signals of the spin-orbit split core level edges [6]. In XAS, a core level electron is excited into a magnetic valence state and the dipole selection rules, coupled with the Pauli exclusion principle, give a difference in the absorption probability of left and right circularly polarized light so that only electrons with specific spin and orbital magnetic quantum numbers can be excited into the empty valence states. It has been said that XAS measures the 'amount' of core holes created [6]. Circular magnetic X-ray dichroism (CMXD) is a useful probe of the orientations and size of the local magnetic moments in rare earths [7]. The open valence shells have a predominantly atomic character and the absolute value of the local moment is approximately that of the free ion since there is no quenching of the orbital moment.

Dichroism measurements using soft X-rays have several advantages over using photons in other energy regions [8]. The soft X-ray region (200-1500eV) gives access to the strong dipole-permitted core 3d to valence 4f excitations of the rare earths and it is the 4f states that are responsible for most of the magnetic properties. The disadvantage of using hard X-rays (>3keV) is that the 4f states can only be reached through the weak quadrupole transitions from the 2p core level of rare earths. The broad natural linewidth of the 2p core levels also tends to smear out the fine structure in absorption and MCD spectra. A disadvantage of using photons in the VUV region (<200eV) where the MCD can be measured through the strong dipole-permitted core 4d to valence 4f excitations of the rare earths is that the unresolvable spin-orbit splitting of the 4d_{3/2} and 4d_{5/2} levels makes the data analysis difficult.

CMXD allows for element-specific analysis of magnetic compounds and multilayers by choosing a photon energy corresponding to an absorption edge of the element in question. There are three important factors of dichroism which are recognised in the one-electron model [9] which takes into account the spin-polarization of the excited electron due to inner shell spin-orbit coupling (the so-called Fano effect) as well as the spin-split density of the final states at and above the Fermi level. These three factors are;

(a) the exchange interaction is the driving force of long-range spin order,

(b) use of circularly polarized light with preferential propagation along the magnetic quantization axis,

(c) spin-orbit interaction provides the mechanism for an effective coupling between the angular momentum of the circularly polarized photon and the magnetically ordered electron spins.

In CMXD experiments the differences in the absorption of left- and rightcircularly polarized light are measured as the energy of the incident light is swept across the an absorption edge in a material with a net magnetic moment. The orbital part of the magnetic moment, μ_L , in magnetic materials is determined by the interplay of several effects [10] – Coulomb and spin-orbit interactions, hybridization and crystal fields. To study these effects the independent determination of μ_L and μ_S (the spin contribution) is of great importance. In neutron scattering the two contributions can be separated by fitting the measured form factors with a suitable model. In non-resonant X-ray diffraction, different responses to polarization can, theoretically, separate spin and orbital densities, but experimental attempts have so far failed to implement a quantitative separation. Sum rules have been derived [10, 11] relating the integrated intensities of the spin-orbit-split multiplets in the absorption spectra to the expectation values of the orbital angular moment operator, $\langle L_Z \rangle$, spin magnetic moment operator, $\langle S_Z \rangle$, and dipole moment operator, $\langle T_Z \rangle$. These sum rules are discussed in later sections of this chapter.

7.3 3d4f XAS of Rare Earth Metals

As stated in §2.3, the distinguishing feature of the rare earths in the solid state is the atomic character of the 4f orbitals which lie within the ion, yet have low binding energies. As a consequence, many solid state and gas-phase spectroscopies involving the 4f electrons can be explained with the multiplet structure obtained from atomic calculations. In the upper panels of figure 7-1 [7] are shown the calculated 3d absorption spectra of trivalent Gd³⁺. The absorption process involves the excitation of a 3d core electron into the 4f shell where all the other shells are either filled or empty.



Photon Energy (eV)

Figure 7-1.

The upper panels show the calculated $3d \rightarrow 4f$ X-ray absorption spectra of trivalent Gd. The curves denote the absorption cross-sections of the $3d_{5/2}$ (left hand panel) and $3d_{3/2}$ (right hand panel) groups. The scale is Å². These spectra were obtained from the oscillator strengths (plotted on an arbitrary scale as vertical bars) which were convoluted with lineshapes representing the lifetime of the 3d core hole (Lorentzian) and the instrumental broadening (Gaussian).

The lower panels show the same curves with the vertical scale of the $3d_{3/2}$ expanded, showing the contribution of each ΔJ group to the total spectrum $(-\cdot-\cdot \rightarrow \Delta J=-1, \quad -- \Rightarrow \Delta J=0, \quad \cdots \Rightarrow \Delta J=+1)$.

Generally

$3d^{10}4f^n|\alpha JM\rangle \rightarrow 3d^94f^{n+1}|\alpha' J'M'\rangle$

and in the case of Gd³⁺, $3d^{10}4f^7 |\alpha JM\rangle \rightarrow 3d^94f^8 |\alpha' J'M'\rangle$.

The final-state configuration contains two open shells and consequently forms a complex multiplet which is divided, by spin-orbit splitting, into $3d_{3/2}$ and $3d_{5/2}$. Of the many thousands of transitions possible between Zeeman components, only those that can be reached from the ground state obeying the selection rules ($\Delta J=0, \pm 1, \Delta M=0, \pm 1$) are present in the absorption spectrum, so that the actual spectral shape reflects only a subset of the total final state multiplets. The subset depends critically on the nature of the initial state |JM⟩. The deformation from spherical symmetry of the 4f shell, from which the dichroism has to originate, was assumed to originate from the influence of magnetic interactions, that is the Zeeman splittings, on the initial |JM⟩ state. The disadvantage of this approach is that the role of crystal electric fields is neglected. These crystal fields can also break the spherical symmetry of the 4f shells, but are much less important in the rare earths than in the 3d transition metals where they dominate the multiplet structure.

Transitions to the unoccupied 5p continuum states are allowed but, near the absorption edge, have negligible cross-section compared to the $3d \rightarrow 4f$ transitions and can be ignored [7]. The lower panels of figure 7-1 are the same spectra as in the upper panels, but with the vertical scale of the $3d_{3/2}$ group expanded and the spectra have been separated into the three contributions formed by the selection rules $\Delta J=0, \pm 1$.

There has been previous work looking at the $M_{4,5}$ absorption edge of Gd with circularly polarized light [12] though the material studied in this case was a gadolinium iron garnet, $Gd_3Fe_5O_{12}$. Two dipole permitted absorption lines were measured – the $2p\rightarrow 3d$ excitation of Fe and the $3d\rightarrow 4f$ transition of Gd. The $Gd_3Fe_5O_{12}$ garnet has the following magnetic structure: two sublattices of ferric (Fe³⁺) ions which are antiferromagnetically coupled by superexchange through the oxygen atoms, and the Gd^{3+} ions which are antiferromagnetically coupled through superexchange to the net moment of the Fe³⁺ ions, but this coupling is much weaker than that among the Fe³⁺ ions. This compares with the work presented here where it will be shown that ultrathin Gd films couple antiferromagnetically with ultrathin Fe films.

The Gd M_{4,5} CMXD spectra taken by Rudolf *et al* [12] are markedly temperature dependent and, surprisingly, change sign on cooling from 300K to 77K. At 300K the dichroism is positive at the M₅ line and negative at the M₄ line. As is the case with Fe, the sign of the magnetic circular dichroism can be related to the orientation of the magnetic moment of Gd. One expects a negative MCD at the M₅ edge and a positive MCD at the M₄ edge for 3d \rightarrow 4f transitions if the atom's magnetic moment is aligned parallel to the external magnetic field. The observation of a positive MCD signal at the M₅ edge confirms a residual antiferromagnetic coupling between the Gd³⁺ ions and the net magnetic moment of the Fe lattice. At low temperature, however, the dichroism changes sign in agreement with the reversal of the local magnetic orientation when the compensation point is reached. That is, at room temperature the Fe lattices dictate the ferrimagnetic properties of the material and the Gd ions are essentially disordered, but at lower temperatures the Gd lattice becomes ordered. Since the Gd magnetic moment is much larger than the net magnetic moment of the Fe lattices (approximately $21 \mu_B$ per formula unit compared to $\sim 5 \mu_B$ for Fe) there exists a certain compensation temperature (288K) at which the macroscopic magnetization flips direction. At 77K the magnitude of the MCD signal is about a factor of 4 greater than at 300K.

7.4 Magnetic Dichroism in X-ray Absorption Spectra

In the presence of a magnetic field **H** parallel to the z-axis, both the initial and the final states are split into their Zeeman components with an energy separation $-g\mu_BHM$. From figure 7-2 [7], the degenerate $\Delta J = -1$ line consists of 3 groups of lines with equal ΔM . The dots below the lines indicate their relative amplitudes. The occupation of the levels M of the initial state is dictated by a Boltzmann distribution, so the upper levels are relatively depopulated and the absorption by these levels will diminish. This causes the absorption strength of the ΔM groups to become unequal, resulting in different absorption coefficients for different polarizations. It is clear that when T=0K only the $M = -\frac{7}{2}$ level is occupied, so the ΔM =1 transition (indicated by the solid line) is the only possible transition, stimulated only by left circularly polarized radiation. It follows that there can be no absorption of right circularly polarized light at T=0K.

The orbital part of the magnetic moment, μ_L , in magnetic materials is determined by the interplay among several effects, i.e. Coulomb and spin-orbit interactions, hybridization and crystal fields. To study these effects it is important to be able to determine independently μ_L and μ_S . Thole *et al* have shown that it is possible to directly measure the ground state expectation value of the orbital angular momentum operator, $\langle L_Z \rangle$ by core level absorption spectroscopy [10]. This is achieved by considering the difference between the integrated absorption intensity for right and left circularly polarized light. This integral of the absorption peaks has to be taken over the complete (background subtracted) core level edge of magnetically oriented materials. To obtain the expression, the integrated difference spectrum must be normalized to the unpolarized absorption spectrum,

$$\rho \equiv \frac{\int d\omega (\mu^{+} - \mu^{-})}{\int d\omega (\mu^{+} + \mu^{-} + \mu^{0})} = \frac{1}{2} \frac{c(c+1) - \ell(\ell+1) - 2}{\ell(\ell+1)(4\ell+2 - n)} \langle L_{Z} \rangle$$
(7-1)



Figure 7-2. Energy level diagram of the transition of Yb^{3+} with (right) and without (left) a magnetic field. The transitions that are allowed by the optical dipole selection rules are indicated by the arrows. Their relative intensities are given by the dots.

The polarization of the light with respect to the magnetic field **H** required for the different ΔM channels is indicated at the bottom.

Only the line of the ΔM =+1 channel is allowed at 0K, and is indicated by the solid arrow.
where c refers to the quantum number ℓ of the core hole and ℓ refers to the excited level. n is the initial number of electrons in the final state level or, alternatively $(4\ell + 2 - n)$ is the number of holes in the 4f band before excitation. $\langle L_Z \rangle$ is in Bohr magneton units.

Experimentally, the determination of $\langle L_Z \rangle$ requires the measurement of the absorption spectra, on a magnetic material, with the field B parallel (μ^+), antiparallel (μ^-), and perpendicular (μ^0) to the photon angular momentum, but it can be taken as a reasonable assumption that $\mu^0 = \frac{1}{2}(\mu^+ + \mu^-)$ which leads to

$$\rho = \frac{\int d\omega(\mu^{+} - \mu^{-})}{\frac{3}{2} \int d\omega(\mu^{+} + \mu^{-})} = \frac{1}{2} \frac{c(c+1) - \ell(\ell+1) - 2}{\ell(\ell+1)(4\ell+2 - n)} \langle L_{Z} \rangle$$
(7-2)

This expression was applied by Thole [10] to CMXD data obtained at the $M_{4,5}$ edges of Fe₅Gd₃O₁₂ by Rudolf *et al* [12], where the 4f⁷ ground state configuration of Gd³⁺ implies $\langle L_Z \rangle = 0$. The integrated CMXD data obtained by Rudolf *et al* confirm this, and give values of $\langle L_Z \rangle = 0.00$ (± 0.06). So, Thole *et al* have derived an approximate magneto-optical sum rule relating the integrated CMXD spectra of a core hole to the ground state expectation value of a shell-specific orbital magnetization. However, we will show that ultrathin Gd films deposited onto Fe buffer layers do show a dichroic effect, and hence a non-zero value for $\langle L_Z \rangle$.

Further work by Carra *et al* [11] derived more sum rules applicable to CMXD data relating the CMXD signal, integrated over a single partner of a spin-orbit-split core level edge, to the ground state expectation values of the operators that describe the magnetic field generated by the valence electrons, specifically the total spin operator $\langle S_z \rangle$ and the magnetic dipole operator $\langle T_z \rangle$.

The ground state expectation value of the spin-dependent part of the local magnetic field per hole is given by,

$$\delta = \frac{\int_{j_{+}}^{(\mu^{+} - \mu^{-})d\omega - \left[\frac{c+1}{c}\right]\int_{j_{-}}^{(\mu^{+} - \mu^{-})d\omega}}{\int_{j_{+}+j_{-}}^{j_{+}+\mu^{-} + \mu^{0})d\omega}}$$
$$= \frac{\ell(\ell+1) - 2 - c(c+1)}{3c(4\ell+2-n)} \langle S_{z} \rangle$$
$$+ \frac{\ell(\ell+1)[\ell(\ell+1) + 2c(c+1) + 4] - 3(c-1)^{2}(c+2)^{2}}{6\ell c(\ell+1)(4\ell+2-n)} \langle T_{z} \rangle$$
(7-3)

In the derivation of these expressions relativistic corrections to the radial part have been neglected. Though this approximation does introduce errors they are generally small. The expectation value of the magnetic dipole operator $\langle T_z \rangle$ provides a measure of the anisotropy of the field of the spins when the atomic cloud is distorted, either by spin-orbit interaction or by crystal field effects.

7.5 Experimental Arrangement

The measurement of magnetic effects in materials is complicated experimentally by the fact that it is necessary that only the sample's magnetism is measured. Every component, except the sample, must be non-magnetic which, in the case of this experiment, meant a complete redesign of the sample heater assembly. The constraints on the new design were that every component had to be non-magnetic and that it was sufficiently narrow to be situated between the two solenoids that were used to provide the sample magnetization. The coils and the sample heater were mounted on independent assemblies with the respective electrical connections entering the UHV chamber through separate ports. The coils were not insulated so it was necessary to provide sufficient clearance for the sample heater so that there was no electrical short circuit.

For this experiment the sample magnetization was achieved via two identical solenoids situated either side of the sample. Each solenoid consisted of ten 10mm diameter turns of standard 1mm diameter copper wire, through which was pulsed a current of 380A over a time interval of 1ms and the solenoids had a separation of 25mm. The current was supplied by a power supply built at the Daresbury SRS specifically for experiments of this nature. The current is sufficiently high to create a magnetic field that can saturate the sample while of short enough duration to avoid heating the copper wire and thus eliminate outgassing from the solenoid. The current supply has a maximum output of 500A but with resistances created at electrical junctions and feedthroughs the achievable maximum was 380A. The magnetic field generated by a solenoid is given by,

$$B = \frac{1}{2}\mu_0 NI \frac{r^2}{\left(r^2 + z^2\right)^{3/2}}$$

For this experiment, r=10 mm, z=12.5 mm, N=10, I=380A. And there were 2 solenoids so the expression needs to be multiplied by 2. Substituting these values gives B=0.1164T. In a vacuum this value can be converted directly to 1164Oe. The coils can also be considered as a pair of Helmholz coils which gives the same result.

A sample heater was designed and built entirely from molybdenum and is shown in figure 7-3. The heater is no more than 20mm wide along its length to eliminate contact



with the magnetisation coils which have a separation of 25mm. The sample cleaning was achieved by electron beam bombardment. A spiral filament wound from 0.25mm diameter thoriated tungsten wire directly under the sample emits electrons which are focused by the tantalum can to radiate the sample evenly. The potential gradient guiding the electrons was formed by applying a 1.5kV potential to the sample while the filament was earthed. A filament current of 6-7A provided an emission current of 100mA, heating the crystal to 2000K.

Circularly polarized light was selected by inserting the beam chopper into the path of the beam to obscure the axial part of the beam and select the upper portion of the beam as described in \$3.5.2. The light was incident on the sample at 40° and the emitted photoelectrons were collected around the surface normal by a VSW HA100 analyser. A pair of identical solenoids (10 turns of 1mm diameter high purity copper wire) either side of the sample provided a magnetic field of 1420 Oe, sufficient for sample magnetization [12]. All spectra were taken with the sample at room temperature.

CMXD was observed in Gd films of ~2ML thickness which were deposited onto a freshly deposited thin film of Fe. We measured the dichroic effect in the Gd film with varying thickness of the Fe 'buffer' layer, for evidence of any variation in the magnetic order as a function of buffer layer thickness. The cleanliness of the films was checked by monitoring photoemission spectra for the oxygen 2s peak whereby oxygen exposures as low as 0.01 Langmuirs can be detected [9], though an indication of the sample cleanliness could be obtained from the clarity of the features in the SEECC curves. The CMXD spectra were obtained by measuring the sample drain current as a function of photon energy and spectra were taken across the energy range corresponding to the 3d4f excitation. This corresponds to the absorption cross-section of the 3d level as a function of magnetization direction and the shape of the photoabsorption peaks is dependent on whether the incident light is left or right circularly polarized (or, equivalently, when the sample magnetization is reversed), the lineshape being governed by the dipole selection rules. Single spectra encompassing both absorption peaks were taken, but in the analysis each peak was integrated separately because of the limitation of the analysis program ANA which can fit only one Gaussian peak convoluted with a Lorentzian.

7.6 Gd film preparation

All the dichroism measurements were made on Beamline 1.1 at Daresbury SRS. Circularly polarized light was selected as described in §3.6.2, with a degree of polarization of 80% [6]. As described previously, the geometry of the experiment is unchanged if the magnetization of the sample is held constant and the beam polarization is reversed or if the beam polarity is held constant while the sample magnetization is reversed. We used the latter. The SURF1 chamber was used and a base pressure of $6x10^{-11}$ mbar was obtained,

rising to $2x10^{-10}$ mbar during sample deposition. Sample cleaning was carried out as described in §3.7.

Circular magnetic dichroism was not observed in ultrathin Gd films deposited directly onto the Mo(110) substrate which is not surprising since the Curie temperature is critically dependent on film thickness [1]. The Curie temperature reduces as film thickness is decreased until it is $0.4 \times$ the bulk value for films of 5ML thickness. As film thickness is increased the Curie temperature approaches the bulk value, eventually coming within 5% at a thickness of 30-40ML. Since the reduced Curie temperature is in the region of <150K for ultrathin films, the use of a liquid helium cooled sample manipulator is required to cool the sample to a temperature where it is magnetic. The use of a liquid helium cooled manipulator was not possible for this experiment, but magnetism at room temperature could be induced in the sample by depositing ultrathin Gd films onto Fe.

Buffer layers of Fe of varied thickness were deposited first on to the Mo(110) substrate and the ultrathin Gd films were deposited on to the Fe buffer layers. All the depositions were monitored by measuring the net crystal current as explained in §4.3 and features in the SEECC curves can be related to submonolayer structures formed in the Gd adlayer during deposition [14]. SEECC curves obtained during the growth of thick Gd films are shown in figure 7-4. The spectra in figure 7-4 have been offset for clarity and the upper curve was taken when both substrate and adsorbate were least contaminated.

With reference to the upper SEECC curve in figure 7-4, the start of deposition is accompanied by a sharp increase in i_{cc} , with the first maximum at approximately 4.5 minutes. A short decay in the signal is followed by the second maximum at approximately 10 minutes. The value in i_{cc} decays linearly for further deposition until a break at about 22 minutes, followed by further linear decay in the signal. All the SEECC curves show these features, but they become more pronounced as the adsorbate material becomes cleaner through constant outgassing.

Using a calibrated vapour source, features in the SEECC curves obtained during the growth of the Gd film can be correlated with features in Auger spectra and work function measurements obtained by Nicklin [14] and we associate the break in linearity with the completion of a monolayer. Figure 7-5 [14] (below) shows the different ordered overlayer structures observed during the growth of the Gd adlayer. The 1×1 substrate pattern remains for the first 3 minutes when the pattern begins to show $n \times 2$ streaking. Several $n \times 2$ structures are present up to a monolayer. In the later stages of the formation of a monolayer, a $c(5 \times 3)$ structure co-exists with a 4×2 unit mesh. The $c(5 \times 3)$ structure is an open hexagonal arrangement and after the completion of a monolayer the $n \times 2$ order disappears and is replaced by an incommensurate hexagonal pattern.



Figure 7-4. Comparison of SEECC curves between growths as both the Mo(110) substrate and Gd adsorbate become progressively cleaner. (The spectra have been offset for clarity). The top curve was taken during deposition of clean Gd while the bottom curve was taken for deposition of oxidised Gd. Note the peak becomes a doublet as the Gd becomes cleaner.

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Figure 7-5. Chart showing the times at which the different submonolayer structures exist during the deposition of Gd on Mo(110). The monolayer was complete at approximately 14-5 minutes.

Comparing the SEECC curves with the information from the LEED study, it is clear that the rate of deposition is slower than during the LEED study, but it is apparent that the break in linearity at 22 minutes marks the completion of a monolayer and there are no further breaks because the growth of Gd is uneven after the first layer with no ordered structure. The first maximum at approximately 4.5 minutes is associated with the onset of the growth of $n \times 2$ structures. The origin of the second maximum at approximately 10 minutes is less clear though it does coincide with the minimum in work function measurements which mark the onset of the 5×2 submonolayer structure [14]. There is no evidence in the SEECC curves of the onset of the open hexagonal $c(5 \times 3)$ structure.

Gd film depositions were calibrated to the break in linearity at 22 minutes where i_{cc} is decaying with Gd coverage. This point was taken to mark the completion of a monolayer and by extrapolation, a deposition of approximately 90 minutes meant a 4ML coverage of Gd. This was a nominal film thickness with which to monitor the effect of the Fe buffer layer on the Gd film and its variation with the thickness of the Fe.

It should be noted that the SEECC curves taken during the deposition of Fe onto a clean Mo(110) surface showed no detail whatsoever. There was a tiny increase in the value of i_{cc} which peaked after 1-2 minutes before decaying at a rate identical to that of the electron beam before deposition and no structural information was obtainable.

Figure 7-6 shows two curves which contrast the deposition of Gd on the clean Mo(110) substrate with deposition on to an Fe buffer layer, when monitored by SEECC. Both curves peak at approximately 4.5 minutes, but in the case of Gd deposition on to the Fe buffer layer, there is no second maximum. The SEECC signal decays with further deposition and there is no indication of a break in the linearity of the decay to mark the completion of a monolayer. The decay appears to be exponential. It can reasonably be assumed that the growth of the Fe layer is disordered and subsequent deposition of Gd layers will be similarly disordered.



Figure 7-6. SEECC curves taken during the growth of ultrathin Gd films (above) on the clean Mo(110) substrate and (below) on an Fe buffer layer.

The spectra have been offset for clarity. Note the doublet feature of the above curve is lost when Gd is deposited on the Fe buffer layer.

7.7 Results

By comparison with the dichroism in the Fe2p3d absorption spectra it can be seen that the Gd film couples antiferromagnetically with the Fe buffer layer, which agrees with the results of Taborelli *et al* [15] and Camley [16]. The peaks were fitted with Gaussian-Lorentzian lineshapes (representing the instrumental broadening and the lifetime of the 3d hole) to determine the areas under the peaks. These values were then used to calculate the normalised area asymmetry factor similar to that described earlier in §4.9,

$$A_{j} = \frac{\Theta_{j}^{\uparrow\uparrow} - \Theta_{j}^{\uparrow\downarrow}}{\Theta_{j}^{\uparrow\uparrow} + \Theta_{j}^{\uparrow\downarrow}}$$
(7-4)

where $\Theta_j^{\uparrow\uparrow}$ ($\Theta_j^{\uparrow\downarrow}$) refers to the area under each peak with parallel (antiparallel) alignment of the photon spin with the sample magnetization vector. Spectra were taken from 2ML-thick Gd films deposited onto Fe films of thicknesses 2ML and 4ML and the asymmetry factor was found to be proportional to the Fe thickness. The spectra are presented here as;

figure 7-7 Fe2p3d absorption from a 2ML thick Fe film deposited on Mo(110), figure 7-8 Gd3d4f absorption from a 2ML Gd film deposited on a 2ML Fe film, figure 7-9 Fe2p3dabsorption from a 4ML Fe deposited on Mo(110) and figure 7-10 Gd3d4f absorption from a 2ML Gd film deposited on a 4ML Fe film.

With an Fe layer of thickness 2ML, the normalized area asymmetries of the two Gd peaks are calculated to be $A_{5/2}=+0.0173$ and $A_{3/2}=-0.0402$; which change to $A_{5/2}=+0.0203$ and $A_{3/2}=-0.0988$ with an Fe thickness of 4ML. It can be seen that the asymmetry for each peak doubles when the Fe thickness is increased, implying a large increase in the expectation value of the orbital angular momentum.

From the Gd3d4f data, the normalized intensity asymmetry is calculated datum by datum and is plotted in the lower panels of figures. 7-7 and 7-8. \pm 7% for 3d_{5/2} absorption.

The asymmetry curve exhibits this minus-plus character due to changes in the photoabsorption cross-section of the $3d_{3/2}$ and $3d_{5/2}$ levels which results in a change in the peak lineshapes as the magnetization is reversed. The maximum of each absorption peak is shifted by up to 0.5eV. For $3d_{3/2}$ absorption the asymmetry works out at +2%, -3%.



Figure 7-7. Upper panel: Fe2p3d absorption spectra from a 2ML film. The solid line represents parallel orientation of the photon spin with sample magnetization while the dots represent antiparallel orientation. Lower panel: the normalized intensity asymmetry, calculated from the raw data of the upper panel.

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Figure 7-8. Upper panel: Gd3d4f absorption spectra from a 4ML thick Gd film deposited on 2ML Fe. The solid line (dots) represent parallel (antiparallel) alignment of the photon spin with the sample magnetization.

Lower panel: the normalized intensity asymmetry, calculated from the raw data of the upper panel.



Figure 7-9. Upper panel: Fe2p3d absorption spectra from a 4ML thick film. The solid line (dots) represents parallel (antiparallel) orientation of the photon spin with sample magnetization. Lower panel: the normalized intensity asymmetry calculated from the

raw data of the upper panel.





Using equation (7-2) for Gd3d4f absorption, c=2 (3d), ℓ =3 (4f), n=7 (4f⁷), which leads to

$$\rho = \frac{1}{2} \frac{(2 \times 3) - (3 \times 4) - 2}{(3 \times 4) \cdot (12 + 2 - 7)} \langle L_Z \rangle$$
$$= \frac{1}{2} \frac{(6 - 12 - 2)}{12 \times 7} \langle L_Z \rangle = \frac{-8}{168} \langle L_Z \rangle$$
$$\rho = \frac{-1}{21} \langle L_Z \rangle \quad \text{or, } \langle L_Z \rangle = -21\rho$$
(7-5)

And equating the integrals as,

$$\int_{edge} (\mu^+) d\omega = \Theta_{5/2}^{\uparrow\uparrow} + \Theta_{3/2}^{\uparrow\uparrow} \text{ and } \int_{edge} (\mu^-) d\omega = \Theta_{5/2}^{\uparrow\downarrow} + \Theta_{3/2}^{\uparrow\downarrow}$$

It follows that,

$$\rho = \frac{\left(\Theta_{5/2}^{\uparrow\uparrow} + \Theta_{3/2}^{\uparrow\uparrow}\right) - \left(\Theta_{5/2}^{\uparrow\downarrow} + \Theta_{3/2}^{\uparrow\downarrow}\right)}{\left(\Theta_{5/2}^{\uparrow\uparrow} + \Theta_{3/2}^{\uparrow\uparrow}\right) + \left(\Theta_{5/2}^{\uparrow\downarrow} + \Theta_{3/2}^{\uparrow\downarrow}\right)}$$
(7-6)

7.8 Ground State Expectation Value of the Orbital Angular Momentum.

(a) 2ML Fe buffer layer.

From the curve fitting procedures, whereby Gaussian-Lorentz curves were fitted to the absorption peaks, the peak areas with parallel alignment of the magnetization with the photon spin are,

$$\Theta_{5/2}^{\uparrow\uparrow} = 172 \cdot 50(\pm 0 \cdot 02), \quad \Theta_{3/2}^{\uparrow\uparrow} = 94 \cdot 88(\pm 0 \cdot 02)$$

and with antiparallel alignment,

$$\Theta_{5/2}^{\uparrow\downarrow} = 166 \cdot 63(\pm 0 \cdot 02), \quad \Theta_{3/2}^{\uparrow\downarrow} = 101 \cdot 88(\pm 0 \cdot 02).$$

Substituting these values into equation (8-6) gives $\rho = -2.11 \times 10^{-3}$.

Hence, $\langle L_Z \rangle = 0 \cdot 04428$.

(b) 4ML Fe buffer layer.

With parallel alignment of photon spin and magnetization vector,

$$\Theta_{5/2}^{\uparrow\uparrow} = 230 \cdot 20(\pm 0 \cdot 02), \ \Theta_{3/2}^{\uparrow\uparrow} = 108 \cdot 38(\pm 0 \cdot 02)$$

and with antiparallel alignment,

$$\Theta_{5/2}^{\uparrow\downarrow} = 221 \cdot 05(\pm 0 \cdot 01), \quad \Theta_{3/2}^{\uparrow\downarrow} = 132 \cdot 14(\pm 0 \cdot 02).$$

Again, substituting into equation (8-6), $\rho = -0.0211$, and $\langle L_Z \rangle = 0.4432$.

So, when the thickness of the Fe layer is doubled, the expectation value of the orbital angular momentum of Gd in the ground state is increased by a factor of 10. Ultrathin metal layers are known to show properties anomalous to the bulk and their magnetic properties especially are expected to be enhanced in low dimensional structures.

7.9 Discussion.

These results show that the expectation values for the orbital angular momentum are much different to bulk Gd. This should not be surprising since ultrathin films can have significantly different structural, electronic and magnetic properties to the bulk and these ultrathin films are deposited onto a magnetic buffer layer. The magnetisation of the buffer layer will probably induce some magnetic ordering in the overlayer.

In comparison with the work of Rudolf *et al* [12], the presence of Fe induces magnetic moment alignment in the Gd film. Increasing the relative proportion of Fe to Gd causes a stronger alignment of the Gd magnetic moments. Also in comparison with the work of Rudolf *et al*, the dichroism signal is very small at room temperature as shown when the Fe film was 2ML thick and the integrated intensity changed by only 3%.

Since $\langle L_Z \rangle$ is a measure of the z-component of the orbital angular momentum, this suggests that the spins are ordering predominantly in the z-direction when there is a thicker Fe film.

Depositing ultrathin Gd films onto the Fe layer produces a considerably enhanced value for $\langle L_Z \rangle$, and this value increases as the Fe layer increases in thickness.

For bulk Gd the expectation value of $\langle L_Z \rangle$ is zero; however in this case the ultrathin Gd film is deposited on to a layer of Fe. The Fe layer will produce a magnetic field since it was magnetised together with the Gd film by the current pulse through the solenoid. Thus, the Gd film is situated within a magnetic field and this induces the alignment of the Gd magnetic moments.

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Chapter S

Summary and Suggestions For Further Work

- 8.1 Introduction
- 8.2 The Loss of Magnetic Order in Tb Films
- 8.3 The Growth of Gd on Mo(110)
- 8.4 Circular Magnetic X-ray Dichroism in Gd Films

8.5 Suggestions For Further Work

References

8.1 Introduction

This chapter summarises the work presented in this thesis. Section 8.3 deals with the Spin Polarized Photoelectron Diffraction (SPPED) study of ultrathin Tb films deposited on a Cu(001) substrate. Photoemission spectra of the Tb 4s doublet were collected for sample temperatures in the range 80K to 700K and a change in the intensity ratio of the doublet marks the loss of magnetic order. The growth of Gd films on a Mo(110) substrate is reported in section 8.4. The reflected intensity of grazing incidence X-rays varies during deposition and the form of the growth curve provides information about the growth mechanism of the adlayer. Section 8.5 summarises the Circular Magnetic X-ray Dichroism (CMXD) study of ultrathin Gd films. Magnetic order was induced at room temperature by depositing an ultrathin film of Fe on to the Mo(110) substrate before deposition of the Gd film. The expectation value of the angular momentum operator is found to increase as the Fe film is increased in thickness.

8.2 The Loss of Magnetic Order in Tb Films

Terbium has two magnetic phases. Below 220K Tb orders as a basal plane ferromagnet, but between 220K and 230K the system orders as a basal plane spin-wave. The short temperature range over which spin-wave ordering exists suggests that magnetic order may be very sensitive to atomic arrangement.

Spin Polarized Photoelectron Diffraction (SPPED) has been shown to be a useful tool for monitoring magnetic order in single crystals and thin films [1-4]. The advantage of this technique over others is that it requires no external spin detectors, relying on the multiplet splitting in the core level photoemission spectra of magnetic samples. The multiplets are known to intra-atomic in origin [5]. SPPED is used primarily to monitor for the loss of short range magnetic order in a magnetic sample. It is known that long range magnetic order is lost throughout the bulk material when the temperature passes a transition temperature specific to that material, but short range magnetic order can still persist well above the transition temperature.

The study reported in chapter 5 monitors the break down of short range magnetic order in Tb films of nominally 6ML thickness. Photoemission spectra of the Tb 4s multiplet splitting were monitored over the temperature range 80K to 700K and a change in the intensity ratio was observed at $550(\pm 20)$ K. This was attributed to the breakdown of short range magnetic order and occurs at 2.4 times the Néel Temperature for Tb (230K).

The photoemission spectra were fitted with Doniach-Sunjic lineshapes with each of the 4s doublet being fitted with separate contributions. Each of the doublets was fitted with two contributions corresponding to components from interface and surface atoms, but there was no step in the asymmetry factor observed above the noise. However when each of the doublets was fitted with a single contribution, there was a marked step in the value of the asymmetry factor at $530(\pm 20)$ K.

This appears to be in agreement with the theoretical work of Zhang *et al* [6] where they suggest that the transition is due to an enhanced Néel Temperature at the surface. The Tb films in this study were 6ML thick and can be thought of as an isolated surface so this would be consistent with a surface-enhanced Curie Temperature.

8.3 The Growth of Gd on Mo(110)

The deposition of Gd films was monitored using Surface X-ray Diffraction (SXRD) whereby changes in the intensity of the reflected X-ray beam provide information about the growth mode of the adlayer. The X-ray beam was incident on the sample at a grazing angle of 4.5° to the surface plane so that there was almost total reflection.

The Gd films were deposited under a variety of conditions and there was a considerable difference between the growth modes. When deposited at room temperature the growth followed that shown in earlier LEED/Auger studies [7]; that is, the completion of the first monolayer is followed by islanding. The interlayer separation between the monolayer and the Mo(110) surface was found to be 3.15Å and the monolayer coverage was 0.7 (where $\theta = 1$ is the atomic density in the unreconstructed Mo(110) surface).

The growth mode altered considerably when the Mo(110) surface was pre-dosed with pure oxygen. During deposition the intensity of the reflected X-ray intensity was observed to oscillate up to a film thickness of 7ML. Auger spectra collected during deposition showed a gradual decrease in the intensity of the O KLL peak at 510eV suggesting that the oxygen remains at the interface. Improved epitaxial growth in other systems has been observed before. The growth of Ag on Ag(111) [8] improved considerably with the addition of Sb as a surfactant, but in this case the Sb 'floated' up through the adlayers during deposition and the reintroduction of Sb restarted the layer-by-layer growth. Oxygen was used to improve layer-by-layer growth in the growth of Cu on Cu(111) [9]. The epitaxial growth was much improved yet the oxygen remained at the interface. It was suggested that Cu₂O structures formed on the substrate surface providing nucleation sites. In the study presented here it is proposed that Gd_2O_3 sites form on the Mo(110) surface, improving the registry of the adlayer with the substrate. This promotes better layer-by-layer growth because even after the Gd₂O₃ clusters are buried, the influence interlayer transport in subsequent layers. Similar to the growth of Cu on Cu(111), the adsorbed oxygen modifies the kinetics of the growth rather than lowering the activation energy for interlayer diffusion.

The interlayer spacings were found to differ slightly from those values obtained from the depositions at room temperature. The spacing between the substrate and the first monolayer was found to be 3.17Å and the interlayer spacing between the first and second

layers was 6.40Å. The coverage of the first monolayer was calculated to be 0.68 which agrees with a slightly relaxed adlayer incorporating Gd₂O₃ clusters.

The growth of Gd films on to a clean Mo(110) surface showed a consistent trend towards rougher growth as the substrate temperature increased. Up to 300°C the growth curves were distinguished by a sharp peak at the completion of the first monolayer followed by smaller peaks before the reflected X-ray intensity became constant. Above 350°C the growth curves followed the same pattern. The intensity dropped sharply at the start of deposition, reaching a minimum at half a monolayer before rising to a value of constant intensity. This suggests that there is rough growth after the completion of a monolayer, that is Stranski-Krastanov growth.

8.4 Circular Magnetic X-ray Dichroism in Gd Films

Circular Magnetic X-ray Dichroism (CMXD) in absorption spectra is a powerful tool with which to study the magnetic properties of magnetic materials. Sum rules [10, 11] can be utilised to calculate the expectation value of the orbital angular momentum operator, $\langle L_Z \rangle$ and if used in conjunction with Linear Dichroism measurements the expectation values of other quantum operators can be evaluated. The shape of the 3d4f absorption peaks changes when the magnetization of the sample is reversed because selection rules allow only certain transitions depending on the direction of magnetisation or helicity of the incident radiation. The difference in the areas under the peaks for opposite sample magnetisation is proportional to the expectation value of the orbital angular momentum operator.

Magnetism was induced in the Gd films at room temperature by depositing a buffer layer of Fe on to the Mo(110) substrate before deposition of the Gd. The Gd films were of a nominal thickness of 4ML and the expectation value of the orbital angular momentum operator was observed to be dependent on the thickness of the Fe layer. Radiation of a fixed helicity was used and the sample magnetisation was reversed to obtain the dichroic effects.

With a Fe layer of 2ML thickness, the expectation value was calculated to be $\langle L_Z \rangle = 0.0443$ and for a thickness of 4ML, $\langle L_Z \rangle = 0.4432$. There is a ten-fold increase in the expectation value when the Fe buffer layer thickness is doubled to 4ML.

8.5 Suggestions For Further Work

Surfactant-mediated growth of rare earth metal adlayers is an area in which SXRD could be utilised to great effect. The environment of the surface atoms can be deduced from scans of the crystal truncation rods and with the availability of higher intensity synchrotron radiation sources, for example the European Synchrotron Radiation Facility at Grenoble, France, more information can be collected before the sample contaminates. The role of

oxygen in the growth process has only been proposed here, but further study is warranted to determine the exact mechanism and how an effect at the interface can influence growth in subsequent layers.

The magnetic properties of Gd deserve to be treated in more detail with studies extending to other magnetic rare earth metals such as Tb, Dy and Ho. Using both circular polarized light and linear polarized light will allow the calculation of the expectation values of several quantum operators, that is the expectation values of the orbital angular moment operator, $\langle L_Z \rangle$, spin magnetic moment operator, $\langle S_Z \rangle$, and dipole moment operator, $\langle T_Z \rangle$.

Magnetic phenomena in the surface can be very different to that of the bulk so at low coverages the magnetic properties are expected to be heavily influenced by atomic arrangement. Complementing the structural studies with the magnetism studies will provide information on how the magnetic properties vary as adlayer thickness is increased.

The magnetic properties of submonolayer structures are also of interest to the electronics industry. As electrical components become smaller it is important that the magnetic and electronic properties of nanoscopic structures is understood. There can be several atomic structures that exist at some point during the deposition of a monolayer and the electronic and magnetic properties can vary greatly depending on the arrangement of the atoms in the submonolayer adlayer. A comprehensive understanding of these phenomenon would be desirable.

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Appendix A

Sample Preparation

Procedure for electropolishing molybdenum.

The electropolishing solution was made up from 204cm3 of methanol and 85cm3 of concentrated sulphuric acid. The methanol was put into the electropolishing vessel and immersed in an ice bath for 15 minutes. The acid was added very slowly and very carefully to the methanol. The reaction is exothermic and time is allowed for the methanol to settle and cool before adding more acid. This operation was performed in a fume cupboard with the protective glass screen pulled down.

The Mo(110) crystal to be polished was made the anode and suspended in the electropolishing solution on top of a PTFE support with a central column of copper



rod providing the electrical connection.

The cathode was a copper plate wrapped round the inside of the electropolishing bath. A Coutant power supply was used to drive the electropolishing process. In practice, a current of 3A for a time of 3 minutes was sufficient to polish the molybdenum crystal to a bright finish. The voltage varied between 5V and 7V.

After polishing, the crystal was washed in deionised water for several minutes and then ultrasonically washed for 10 minutes in acetone followed by 10 minutes in methanol before being dried with a warm air blower. The ultrasonic washing was necessary to remove all traces of the electropolishing solution.