

Microstructural characterisation of epitaxial rare earth metal based films

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Thesis for the Degree of Doctor of Philosophy

Trinity Term 2000



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Epitaxial rare earth films and superlattices grown by molecular beam epitaxy, MBE, can be designed to investigate theoretical predictions of the magnetic and electronic properties of the metals. These investigations ideally require smooth epitaxial layers with atomically flat interfaces and therefore the microstructure of selected epitaxial rare earth systems has been characterised by a combination of techniques. These systems were grown on a (110) niobium $\parallel$ (11 $\bar{2}$ 0) sapphire substrate. Because the crystallographic quality of the subsequent layers is influenced by the quality of the substrate, the niobium-sapphire interface was studied with transmission electron microscopy, TEM, and high resolution electron microscopy, HREM, to identify uniquely the misfit dislocation network. Conventional TEM specimen preparation techniques were inappropriate for the preparation of metallic foils, and so appropriate specimen preparation techniques were developed. HREM was used to characterise the strain relief mechanisms within a partially relaxed holmium/yttrium superlattice.

Rare earth hydrides are also of interest because of the ability of some rare earths to absorb up to three hydrogen (H) atoms per rare earth atom. Loading between RH_2 (R – rare earth) and RH_3 is completely reversible and the system undergoes a metal-insulator transition. A film subjected to such H-loading is observed to switch from mirror-like to transparent. TEM specimens of RH_2 (R = Ho, Y) were characterised and the structural changes that occur during H-loading were investigated using controlled environment TEM and a combination of scanning probe techniques. The applicability of electron diffraction for the characterisation of structures containing hydrogen is presented. Finally single crystal neutron diffraction techniques have been applied to epitaxial samples of HoD_2 to probe the effect of the addition of extra deuterium atoms on the magnetic properties.

*“For what can be known about God is plain to them,
because God has shown it to them. Ever since the creation of the world
his eternal power and divine nature, invisible though they are, have been
understood and seen through the things he has made”*

Romans 1:19-20

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Publications

Misfit dislocations of epitaxial (110) niobium || (11 $\bar{2}$ 0) sapphire interfaces grown by molecular beam epitaxy,

E. J. Grier, M. L. Jenkins, A. K. Petford-Long, R. C. C. Ward, and M. R. Wells, Thin Solid Films **354**, 94 (2000).

Structural changes to epitaxial (0001) holmium layers during hydrogen loading,

E. J. Grier, O. V. Kolosov, A. K. Petford-Long, R. C. C. Ward, M. R. Wells and B. Hjorvarrrson,

J. Phys. D.: Appl. Phys. **33**, (8) 894 (2000).

Determination of hydrogen ordering within the β -RH_{2+x} phase (R=Ho, Y) using electron diffraction techniques,

E. J. Grier, A. K. Petford-Long, R. C. C. Ward, J. Appl. Cryst. **33**, (5) 1249 (2000).

Magnetism of HoD_{2+x} (x=0,0.21) single crystal films

E. J. Grier, R. A. Cowley, J. P. Goff, S. Hémon, H. Ronnow, R. C. C. Ward, M. R. Wells and B. Hjörvarrrson, *in preparation*

Microstructural characterisation of epitaxial rare earth metals and hydrides (R=Ho, Y)

E. J. Grier, A. K. Petford-Long, R. C. C. Ward, and M. R. Wells, *in preparation*

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Chapter 1

Introduction

The magnetic properties of the rare earths have been the subject of many studies over the last decades because they exhibit such a wide variety of magnetic properties due to the incompletely filled $4f$ electron shell. A comprehensive review of the magnetic properties of rare earth metals has been written recently by Jensen and Mackintosh [1]. Bulk magnetic rare earths have been studied widely in an attempt to understand the underlying mechanisms responsible for the development of a variety of ordered magnetic states and their corresponding phase transitions. It was shown that heavy rare earth metals such as Gd, Dy, Ho and Er exhibit indirect exchange coupling, with conduction electrons mediating the exchange between the highly localised $4f$ electrons, i.e. the Ruderman-Kittel-Kasuya-Yosida or RKKY interaction. However this is sometimes perturbed by anisotropic crystalline fields and magnetoelastic interactions and as the competition between such interactions is temperature dependent, the magnetic phase diagrams are quite complex.

An important advancement in the research of these materials was the synthesis of alloys of the rare earths with the non-magnetic, but chemically related, elements of Y and Lu, for which it was possible to study the crystal field effects in dilute alloys in which the exchange interaction is considerably weaker than the crystal field. However it is extremely difficult to prepare good quality bulk single crystals due to the extreme reactivity of the rare earths and the most important advance in recent years has been the fabrication of single

crystalline thin films and superlattices of rare earths by molecular beam epitaxy, MBE. MBE is an inherently clean process as it uses ultra-high vacuum technology and with such a technique it is possible to design and grow samples of any element or alloy in sequence with different layer thicknesses to enable experimentalists to test directly the theoretical predictions concerning the magnetic and electronic properties of the metals. As the crystal field has a large influence on the magnetic structure of rare earths, the systems are extremely strain sensitive, especially when combined into multilayer stacks. The lattice parameters of the rare earths differ by a few per cent across the series, and so a typical strain within a superlattice system is of order 1% which is sufficient to cause dramatic changes to the magnetic phase diagram [2].

Deposition of high quality monocrystalline films requires a chemically compatible monocrystalline substrate, and the lattice parameters of the deposited films must be within a few percent of those of the substrate surface. The first epitaxial rare earth metal films were grown on single crystal (110) tungsten substrates [3]. The rare earth grows with the [0001] axis normal to the substrate surface. However, metal substrates are very difficult to prepare as the growth surface must be prepared under ultra-high vacuum to avoid chemically adsorbed impurities and oxidation, and the substrates themselves are often of limited crystallographic quality.

In 1986 Kwo *et al.* [4] reported the first single crystal films of yttrium and gadolinium on an α -Al₂O₃ substrate with a single crystal niobium buffer layer inserted. Niobium was chosen as rare earths will grow on the (110) surface of all the bcc refractory metals (as evidenced by the first epitaxial growth of rare earth films on the refractory metal tungsten) and niobium also prevents chemical reactions between the rare earths and the sapphire. Because of the wide availability of high-quality semiconductor substrates there have also been attempts to achieve heteroepitaxial growth of rare earth on lattice matched

buffer films of semiconductors. The LaF_3/GaAs (111) system was used in an attempt to integrate rare earths into semiconductor devices [5] because if rare earths are grown directly onto semiconductor substrates, one or more of the semiconductor elements may diffuse into the metal. By insertion of a layer of rare earth fluoride such reactions were inhibited, and the added possibility of lattice matching the RF_3 (R - rare earth) layer to the rare earth made such substrate systems look interesting for the study of strain within superlattices. Analysis of the free energies suggests that LaF_3 is very stable and the rare earths should be thermodynamically stable in contact with LaF_3 . However, experiments showed that there was evidence for fluorine concentrated in the rare earth film. More recently CaF_2 substrates have been used by Huiberts *et al.* [6]. The deposition of high quality epitaxial films on (111) CaF_2 without a buffer layer has enabled exciting possibilities in the investigation of the electrical resistivity and optical properties of films arising from the transparent, insulating nature of CaF_2 . However, by analogy with the growth on LaF_3 it may be that again F diffusion is a problem with such substrate systems, although work with these substrates is at a relatively early stage and fluorine diffusion has not been explicitly studied.

It is the (110) Nb on $(1\bar{1}20)$ sapphire substrate system that enabled the growth of the first high quality single-crystal metal superlattice of Nb/Ta [7] and it has since been successfully employed as a substrate in MBE growth of rare earth [8-10] and transition metal superlattices [11] and most recently, for epitaxial films of Laves phase intermetallic compounds [12]. Chapters 2 and 3 introduce the crystallography of the rare earths and the growth techniques employed and the orientation relationship of epitaxial rare earth systems grown on a (110) Nb || $(1\bar{1}20)$ sapphire substrate system. Chapter 4 outlines the basic theory underlying the techniques employed in the characterisation studies described in this thesis.

The aim of this thesis was the characterisation of the atomic structure of rare earth metal thin films and superlattices, applying the technique of high resolution microscopy,

HREM, to these systems for the first time, in order to correlate the microstructure of the material with the observed physical properties. Hitherto the work by the group in Oxford has employed the techniques of x-ray and neutron diffraction for structural and magnetic characterisation of rare earth thin films and superlattices [13-16] with great success. The application of HREM to such systems would enable for the first time a direct view of the atomic nature of the systems, especially important in the understanding of the strain relief mechanisms within the epitaxial films. At every interface within the superlattice, the lattice parameters of the two materials differ and strain develops within the material which must be relieved. Usually this strain relief is achieved either by the introduction of defects, such as dislocations, or by roughening of the surface. Understanding the strain relief mechanisms and their influence on the film morphology is of primary importance.

As already mentioned the (110) Nb on $(11\bar{2}0)$ sapphire substrate system is used widely for the growth of rare earth and transition metal single crystals. For successful studies of the magnetic properties of such systems, smooth epitaxial layers with atomically flat interfaces are required, and inevitably the quality of the niobium layer will influence how well the rest of the structure will grow. Thus for a complete study of the atomic structure of rare earth thin films and superlattices it is first necessary to characterise the substrate system on which they are grown. Chapter 5 presents a combination of reflection high-energy electron diffraction, RHEED, HREM, and conventional transmission electron microscopy, CTEM, studies of the $(110)_{\text{Nb}} \parallel (11\bar{2}0)_{\text{Al}_2\text{O}_3}$ interface, with the aim of characterising the coherent regions of the interface and uniquely identifying the nature of the misfit dislocations.

The techniques used in the transmission electron microscopy, TEM, specimen preparation highlighted the extreme reactivity of the rare earths, as conventional TEM specimen preparation techniques [17] have not proved successful for producing specimens

representative of the initial bulk metal sample. TEM specimens were seen to exhibit (as seen in typical diffraction patterns) a range of crystallographic structures including the RH_2 and R_2O_3 phases with these structures thought to form during specimen preparation. However, Chapter 6 reports the first successful HREM study of holmium and yttrium metal thin films and superlattices, with TEM samples representative of the metal α -phase prepared by the use of a focused ion beam, FIB, system.

The highly reactive nature of the rare earths, as highlighted in the TEM specimen preparation, was well known from previous rare earth metal preparation. The problem is exacerbated in thin films with their large ratio of surface area to volume, and a reliable method of passivation is required [18]. Although it was not possible to passivate the TEM specimens prepared by conventional specimen preparation techniques the specimens of RH_2 were of considerable interest in their own right, due to the report in 1996 by Huiberts *et al.* [19] that rare earth metal-hydride films exhibit spectacular changes in the optical and electrical properties as the hydrogen concentration changes. They reported that shiny, metallic dihydride films of yttrium, lanthanum and rare earths became transparent in the visible part of the optical spectrum upon transformation to the trihydride. This is a result of the fact that rare earth elements are able to absorb up to 3 hydrogen atoms per metal atom, and so during hydrogen loading there is a continuous decrease in the carrier density, which gives rise to a metal-insulator transition in the interval between RH_2 and RH_3 . The loading is reversible and the switching time between mirror and transparent film is of the order of a fraction of a second for polycrystalline samples [20]. The systems are of interest both for the practical applications of switchable mirrors, and because of the possibility of real-time visualisation of hydrogen migration in metals [21].

Studies of the hydrogen loading and switching of *epitaxial* films of (0001) Y on (110) Nb or (110) W have been reported by Wildes *et al.* [18], Remhof *et al.* [22] and

Hayoz *et al.* [23], and of (0001) Y on (111) CaF₂ by Nagengast *et al.* [6]. These studies have shown that the single crystal nature of the films is preserved throughout the cycling between the α , β and γ phases, accommodating the changes of structure of the rare earth metal lattice (hcp (α) - fcc (β) - hcp (γ)). There are conflicting reports, however, about the extent of the deterioration in crystalline perfection which occurs as a result of loading/unloading cycles. Chapter 7 looks in detail at the structural changes which occur during hydrogen loading of thin epitaxial films of holmium.

The presence of hydrogen leads to a range of other interesting properties. A comprehensive review of the properties and behaviour of R-H systems has been given by Vajda [24]. The β -phase dihydride exists over a considerable range of hydrogen concentration. In the range RH_{2+x} the excess H atoms are effectively in solution in the RH_{2+x} lattice and occupy the octahedral sites (*o*-sites) within the unit cell. When the structures are cooled below their mobility limits, the octahedral hydrogens atoms can form short-range ordered (SRO) and long-range ordered (LRO) structures. At higher temperatures the RH_{2+x} system may be considered as a lattice gas in which the excess hydrogen atoms randomly occupy the octahedral interstices of the fcc lattice. The ordering has been observed to give rise to anomalies in many of the physical parameters including anomalies in the thermal behaviour of the lattice parameter [25], the eventual metal-insulator, M-I, transition that occurs in these systems [26] and in the magnetic properties.

As part of the study of the structural changes which occur during hydrogen loading of thin films, high resolution electron microscopy, HREM, was used as a characterisation tool. However, as already mentioned the rare earths are extremely reactive and specimens exhibit a range of crystallographic phases, and even after confirming the presence of such structures as RH₂ and R₂O₃ phases by their diffraction patterns there still remained unidentified diffraction spots in the patterns. As a process of elimination of possible

structures present in the specimens, computer simulations of the diffraction patterns from hydrogen ordered structures were performed and the results of the simulations and a discussion of the applicability of electron diffraction techniques in the characterisation of hydrogen ordering in rare earths are presented in Chapter 8.

The effect of the excess hydrogen atoms on the magnetic properties of single crystal films of HoD_{2+x} ($x=0,0.21$) is investigated in Chapter 9. The decrease in conduction electron density upon hydrogen absorption will diminish the magnetic manifestations that are dependent on the RKKY interaction. The ordering into sublattices at low temperatures can also change the magnetic properties dramatically by modifying the local site symmetry. For example a rare earth atom site within the unit cell with all neighbouring octahedral sites vacant has a very different symmetry from when one octahedral site is occupied by hydrogen. Thus the crystal field and magnetic properties of the dihydrides can be expected to change as the $[\text{H}]/[\text{R}]$ value varies.

References

- [1] J. Jensen and A. R. Mackintosh *Rare earth Magnetism: Structures and Excitations*, Oxford University Press, New York, (1991).
- [2] C. P. Flynn and M. B. Salamon "Synthesis and properties of single-crystal nanostructures", in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 22, edited by K. A. Gschneidner and L. Eyring, Elsevier Science,,(1996).
- [3] D. Weller and S. F. Alvarado, *Appl. Phys.* **59**, 2908 (1986).
- [4] J. Kwo, M. Hong, and S. Nakahara, *Appl. Phys. Lett.* **49**, 319 (1986).
- [5] R. F. C. Farrow, S. S. P. Parkin, and V. S. Speriosu, *Appl. Phys.* **64**, 5315 (1988).

-
- [6] D. G. Nagengast, J. W. J. Kerssemakers, A. T. M. van Gogh, B. Dam, and R. Griessen, *Appl. Phys. Lett.* **75**, 1724 (1999).
- [7] S. M. Durbin, J. E. Cunningham, M. E. Mochel, and C. P. Flynn, *J. Phys. F: Met. Phys.* **11**, (1981).
- [8] J. Kwo, E. M. Gyorgy, D. B. McWhan, M. Hong, F. J. DiSalvo, C. Vettier, and J. E. Bower, *Phys. Rev. Lett.* **55**, 1402 (1985).
- [9] M. B. Salamon, S. Sinha, J. J. Rhyne, J. E. Cunningham, R. W. Erwin, J. Borchers, and C. P. Flynn, *Phys. Rev. Lett.* **56**, 259 (1986).
- [10] D. F. McMorrow, D. Jehan, P. P. Swaddling, R. A. Cowley, R. C. C. Ward, M. R. Wells, and K. N. Clausen, *Phys. B* **192**, 150 (1993).
- [11] P. Bodeker, A. Abrometi, K. Bohl, P. Sonntag, N. Metoki, and H. Zabel, *Phys. Rev. B* **47**, 2353 (1993).
- [12] V. Oderno, C. Dufour, K. Dumesnil, P. Mangin, and G. Marchal, *J. Cryst. Growth* **165**, 175 (1996).
- [13] P. P. Swaddling, D. F. McMorrow, R. A. Cowley, R. C. C. Ward, and M. R. Wells, *Phys. Rev. Lett.* **73**, (1994).
- [14] D. Jehan, D. F. McMorrow, R. A. Cowley, R. C. C. Ward, M. R. Wells, N. Hagmann, and K. N. Clausen, *Phys. Rev. B* **48**, 5594 (1993).
- [15] D. F. McMorrow, P. P. Swaddling, R. A. Cowley, R. C. C. Ward, and M. R. Wells, *J. Phys. C* **6**, 6553 (1996).
- [16] C. de la Fuente, R. A. Cowley, J. P. Goff, R. C. C. Ward, M. R. Wells, and D. F. McMorrow, *J. Phys. C* **11**, 6529 (1999).
- [17] S. B. Newcomb, C. B. Boothroyd, and W. M. Stobbs, *J. Mic.* **140**, 195 (1985).
- [18] A. R. Wildes, R. C. C. Ward, M. R. Wells, and B. Hjorvarsson, *J. Alloys and Compounds* **242**, 49 (1996).

-
- [19] J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, *Nature* **380**, 231 (1996).
- [20] P. van der Sluis, *Appl. Phys. Lett.* **73**, 1826 (1998).
- [21] F. J. A. den Broeder, S. J. van der Molen, M. Kremers, J. N. Huiberts, D. G. Nagengast, A. T. M. van Gogh, W. H. Huisman, N. J. Koeman, B. Dam, J. H. Rector, S. Plota, M. Haaksma, R. M. N. Hanzen, R. M. Jungblut, P. A. Duine, and R. Griessen, *Nature* **394**, 656 (1998).
- [22] A. Remhof, G. Song, C. Sutter, A. Schreyer, R. Siebrecht, and H. Zabel, *Phys. Rev. B* **59**, 6689 (1999).
- [23] J. Hayoz, S. Sarbach, T. Pillo, E. Boschung, D. Naumovic, P. Aebi, and L. Schlapbach, *Phys. Rev. B* **58**, R4270 (1998).
- [24] P. Vajda "Hydrogen in rare-earth metals, including RH_{2+x} phases", in *Handbook on the physics and chemistry of rare earths, Vol. 20*, edited by K. A. Gschneidner Jr. and L. Eyring, Elsevier Science,, 208 (1995).
- [25] M. Chiheb, J. N. Daou, and P. Vajda, *Z. Phys. Chem.* **179**, 271 (1993).
- [26] P. Vajda and J. N. Daou, *Phys. Rev. Lett.* **66**, 31763178 (1991).

Chapter 2

Properties of the Rare-Earth Elements

This chapter outlines the structural properties of the rare earth elements that are considered in this thesis. Section 2.2 describes the crystallography of all the systems investigated, with section 2.2.1 describing the rare earth metal structures and section 2.2.2 the phases within the rare earth metal – hydrogen system.

2.1 Introduction

The rare earths are the group of elements with atomic number from 58 to 71. They are all characterised by possessing an incomplete atomic shell of $4f$ electrons, surrounded by the same valence configuration of electrons, consisting of two $6s$ and one $5d$ electrons. The $4f$ shell is progressively filled on moving across the group with the $4f$ shell empty for La and completely filled for Lu. Y and Sc are often grouped with the rare earths, even though they have no $4f$ electrons, because they have similar valence shell configurations consisting of two s electrons and one d electron, and hence similar chemical properties. The $4f$ electrons remain highly localised on the atoms and have little effect on the chemical properties of the rare earths, although they considerably affect the magnetic properties. The "heavy" rare earths are the elements with a $4f$ shell that is more than half full, and the "light" rare earths have a $4f$ shell that is less than half full. Holmium is thus a heavy rare earth, and yttrium is observed to be similar to the heavy rare earths.

2.2 Crystallography

2.2.1 Metal structure

Because of the similar valence shell configurations the main structural properties of the rare earths are similar, with all elements exhibiting a close packed structure [1]. In common with most of the heavy rare earths, holmium and yttrium form the hexagonal close-packed, hcp, $P6_3/mmc$ structure with lattice constants as summarised in Table 2.1. The crystal structure is illustrated in Figure 2.1(a). The metal atoms occupy the positions $(0, 0, 0)$ and $(1/3, 2/3, 1/2)$. The stacking sequence for an hcp metal along the c -axis is given by $AB\dots$ with each letter denoting an identical hexagonal plane of atoms. The other close-packed structures exhibited by the rare earths are a double hexagonal close-packed, dhcp, structure with stacking $ABAC\dots$ for elements with $Z < 64$, the Sm-structure $ABABCBCAC\dots$, and face-centre cubic, fcc, stacking $ABC\dots$ for γ -Ce and Yb. The hcp and fcc structures, relevant to this work, are shown in Figure 2.1, with the close-packed planes shaded.

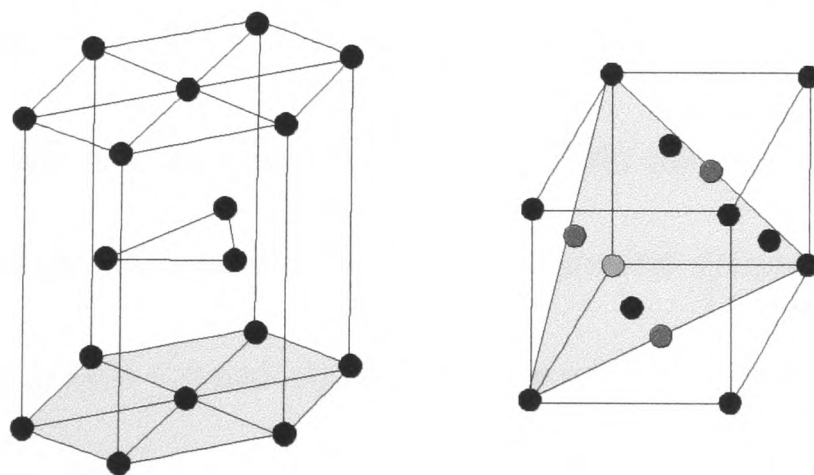


Figure 2.1: (a) hcp structure (b) fcc structure. The close packed planes $(0001)_{\text{hcp}}$ and $(111)_{\text{fcc}}$ are indicated by the shading

2.2.2 The R-H metal system

Among different hydrogen-metal systems, rare earth metals (including holmium and yttrium) are of special interest because of their ability to absorb up to 3 H atoms per metal atom [2]. This leads to dramatic changes in the physical properties of the system. The R-H phase diagram involves three different crystallographic structures, (α , β , γ) and the phase diagrams for Ho-H [3] and Y-H [4] are shown in Figure 2.2.

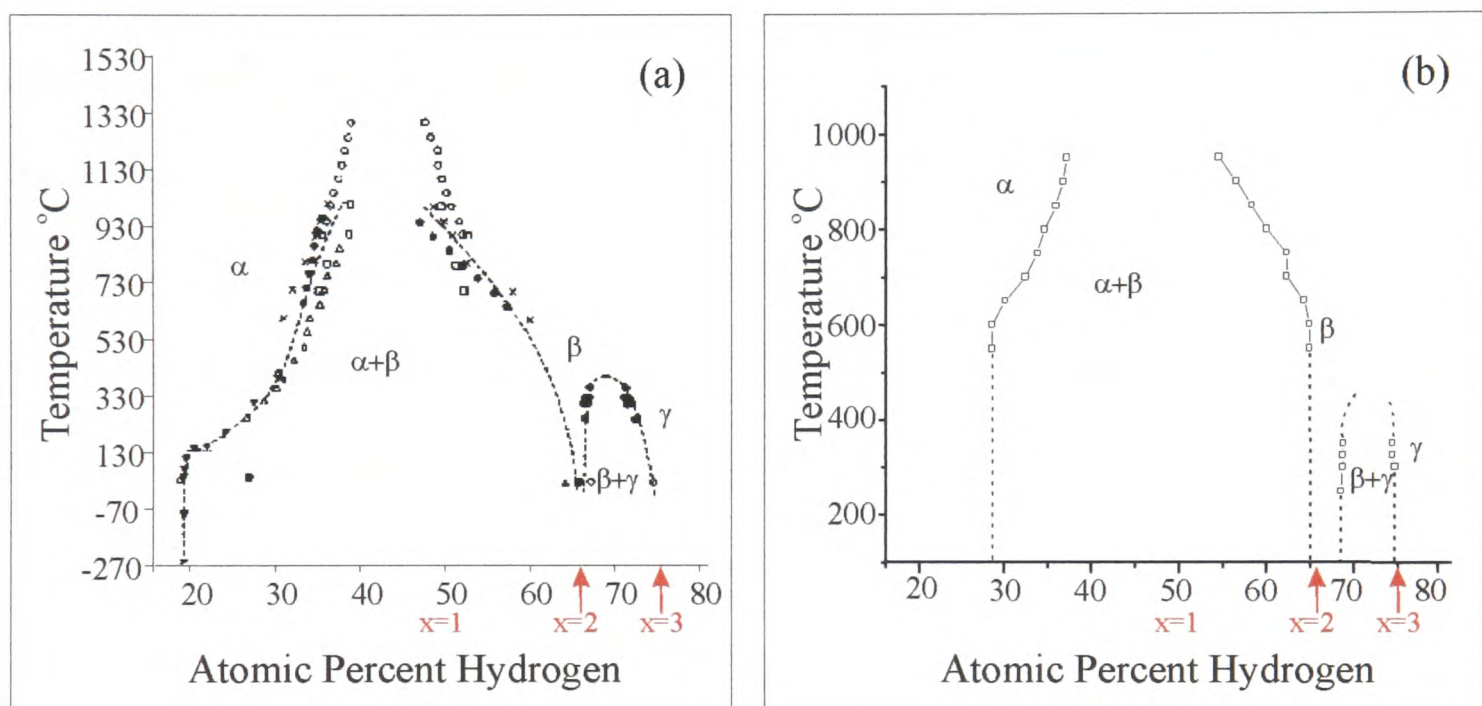


Figure 2.2: (a) Y-H phase diagram (b) Ho-H phase diagram

2.2.2.1 α -phase

The α -phase is a metallic solid solution, with the H atoms randomly occupying the interstitial sites of the host metal lattice with tetrahedral symmetry (t -sites) i.e. $(0, 0, \frac{1}{4}-z)$, $(0, 0, \frac{3}{4}+z)$, $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4}+z)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4}-z)$ with $z = -(1/3)(c/a)^2$. For the heavy rare earths and yttrium there is a metastable phase at low temperature where the hydrogen sublattice is ordered. The α -phase of yttrium orders below 400°C; similar measurements have not been performed on the holmium system.

2.2.2.2 β -phase

The dihydride phase of the heavy rare earths crystallises in the fcc fluorite type structure $Fm\bar{3}m$, in which ideally all the tetrahedral interstitial sites of the fcc metal lattice are filled with hydrogen, as shown in Figure 2.3(a). This lattice is significantly expanded with respect to the α -phase, by 5% for Y and by 8.7% for Ho. This expansion is accompanied by a rearrangement of the stacking sequence, where the hcp AB... close packed plane stacking becomes an ABC... stacked close packed crystal. The β -phase dihydride exists over a considerable range of hydrogen concentration. In the range RH_{2+x} the excess H atoms are effectively in solution on the octahedral interstitial sites of the fcc dihydride lattice, shown in figure 2.3(b), and are free to interact and form H sublattices [5]. This ordering is observed as an anomaly in several physical properties [6,7] and is discussed in more detail in chapter 8. The pure dihydride phase exists for hydrogen concentrations $-0.15 \leq x \leq 0.17$ (Ho) and $-0.2 \leq x \leq 0.1$ (Y) where x is defined in RH_{2+x} . Above the maximum concentration the hcp γ -phase trihydride begins to form. The dihydride phase has metallic properties which gradually disappear as the system approaches the trihydride.

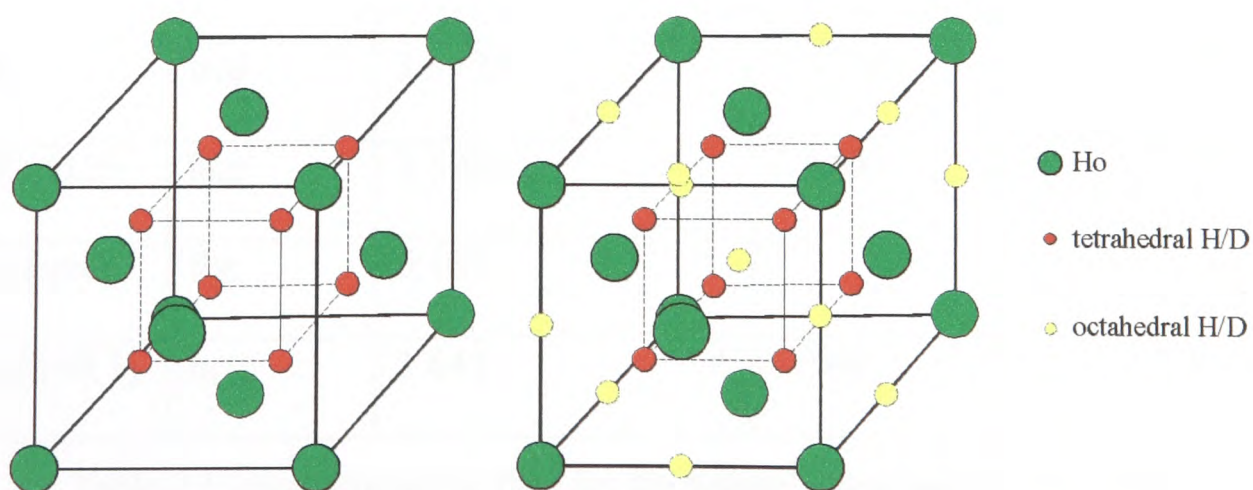


Figure 2.3: (a) fcc lattice showing the position of the tetrahedral interstitial sites, that are ideally occupied for stoichiometric RH_2 (b) fcc lattice showing the position of the tetrahedral and octahedral interstitial sites. The octahedral sites are randomly occupied in the superstoichiometric RH_{2+x} phase

2.2.2.3 γ -phase

Most R-H systems exhibit a second phase transformation in the hydrogen concentration range $\text{RH}_2 \rightarrow \text{RH}_3$ to the hexagonal γ -phase, which has $\overline{\text{P}}3\text{c}1$ symmetry [8] [9]. The exceptions to this are the divalent lanthanides which do not form trihydrides under normal pressure conditions, and the La-H, Ce-H and Pr-H systems which have a unit cell that is large enough to accommodate 3 hydrogen atoms on the *o*-sites within the β -phase. In the γ -phase the original AB... stacking sequence is regained while the close packed planes are pushed even further apart: the c-axis expansion ($\beta \rightarrow \gamma$) is of order 10% for both Ho and Y.

	Structure	$a(\text{\AA})$ (room temperature)	$c(\text{\AA})$ (room temperature)	c/a ratio ($c/a_{\text{hcp}}=1.633$)
Y metal	hcp	3.6482	5.7318	1.57
$\alpha\text{-YH}_y$ ($y=0.19$)	hcp	3.6636	5.7900	1.58
$\beta\text{-YH}_{2+x}$ ($x=0$)	fcc	5.2095		
$\gamma\text{-YH}_{3-\delta}$ ($\delta=0$)	hcp	3.672	6.657	1.81
Ho metal	hcp	3.5778	5.6178	1.57
$\alpha\text{-HoH}_y$ ($y=0.2$)	hcp	3.5964	5.6667	1.57
$\beta\text{-HoH}_{2+x}$ ($x=0$)	fcc	5.165		
$\gamma\text{-HoH}_{3-\delta}$ ($\delta<0.1$)	hcp	3.642	6.560	1.8

Table 2.1: crystallographic data for the systems investigated in this thesis

References

- [1] R. W. G. Wyckoff *Crystal Structures*, Vol. 1, Interscience, New York, (1965).
- [2] P. Vajda "Hydrogen in rare-earth metals, including RH_{2+x} phases", in *Handbook on the physics and chemistry of rare earths*, Vol. 20, edited by K. A. Gschneidner Jr. and L. Eyring, Elsevier Science, 208 (1995).
- [3] F. C. Perkins and C. E. Lundin, *J. Electrochem. Soc.* **115**, 21 (1968).
- [4] D. Khatamian and F. D. Manchester, *Bull. Alloy Phase Diagrams* **9**, 252 (1988).
- [5] G. André, O. Blaschko, W. Schwarz, J. N. Daou, and P. Vajda, *Phys. Rev. B* **46**, 8644 (1992).
- [6] P. Vajda and J. N. Daou, *Z. Phys. Chem.* **179**, 443 (1993).
- [7] J. N. Daou and P. Vajda, *Phys. Rev. B* **45**, 10907 (1992).
- [8] W. Mansmann and W. E. Wallace, *J. Phys. (Paris)* **25**, 454 (1964).
- [9] N. F. Miron, V. I. Shcherbak, V. N. Bykov, and V. A. Levдик, *Sov. Phys. Crystallog.* **17**, 243 (1972).

Chapter 3

Epitaxial rare earth systems

This chapter discusses epitaxial rare earth systems. Section 3.1 presents the multilayer system that is used for successful single crystal growth of rare earth superlattices, and describes the equipment and experimental conditions necessary to achieve single crystal growth. The crystallography and the orientation relationship of the epitaxial system is discussed in section 3.2. Section 3.3 discusses the factors affecting the film morphology. Firstly the thermodynamic conditions imposed on the system that determine whether or not the system will grow in a 2-D or 3-D growth mode are considered. Secondly the relief of strain within the system by the introduction of misfit dislocations, and simple theories to predict the critical thickness at which it is energetically favourable for such misfit dislocations to form are discussed. Strain relaxation above the critical thickness is also discussed. Finally the relevance of such theories to rare earth epitaxial systems is discussed.

3.1 Growth of epitaxial rare earth systems

Advances in ultra high vacuum deposition demanded by the semiconductor industry have also enabled the growth of metals such as the rare earths by molecular beam epitaxy, MBE. The significant advantage of MBE over other deposition techniques is that it is possible to obtain the source materials with significantly higher purity than sputter targets as no processing of the source materials is required, and it is also possible to outgas the source

materials in-situ in the deposition system under ultra-high vacuum, UHV. Following the first successful single crystal growth of an epitaxial rare earth superlattice system by Kwo *et al.* [1] the multilayer system shown in Figure 3.1 has been used, where for this research rare earth 1 and rare earth 2 are yttrium and holmium respectively. By choosing a sapphire substrate with a $(11\bar{2}0)$ surface plane and inserting a niobium buffer layer to prevent the strong chemical reaction between the rare earth metals and sapphire it is possible to obtain single crystal growth with the (0001) plane of the rare earths lying in the growth plane. In order to relax the misfit strain between the hexagonal close-packed (hcp) rare earths and the body-centred cubic (bcc) niobium, an yttrium seed layer of comparable thickness to the niobium is deposited, and the rare earth superlattice can then be deposited on this seed.

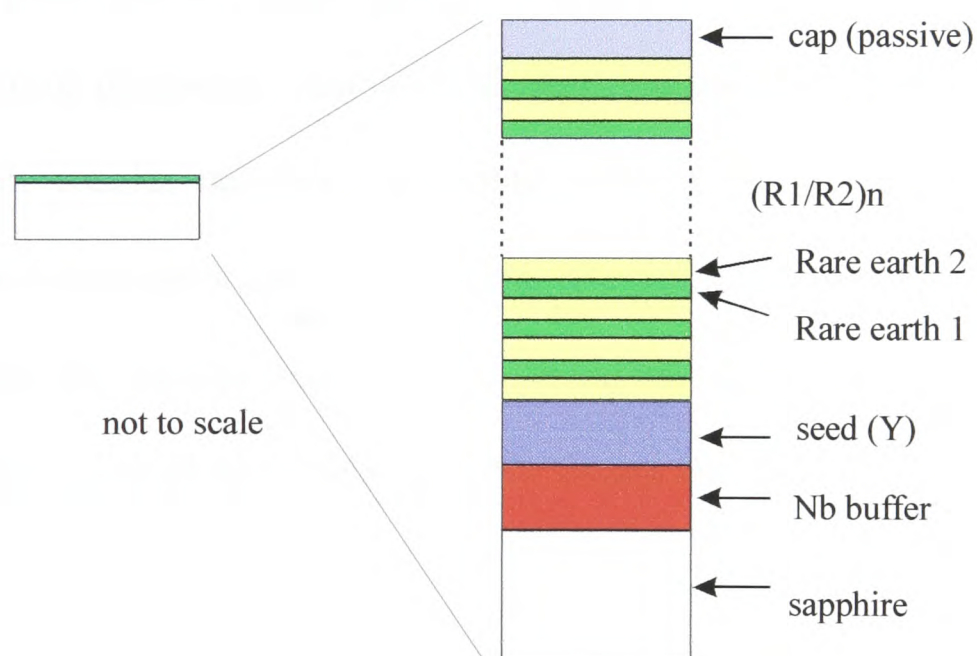


Figure 3.1: Typical superlattice sample

3.1.1 The metal MBE system

The deposition equipment used for this work was a Balzers UMS630 MBE system that is configured with both electron beam and effusion cell sources to cover the wide range of evaporation temperatures of the elements involved.

The vacuum system is composed of two major parts, the growth chamber and the sample introduction (loadlock) chamber as shown in Figure 3.2. In the growth chamber

there are six independent evaporation sources: two standard effusion cells, one high temperature effusion cell and three electron-beam heated sources. In the effusion cell the source material is held in a condensed phase in an inert crucible which is heated by radiation from a resistance-heated filament. A thermocouple provides temperature control to give a flux stability better than $\pm 1\%$. The cell is water cooled to isolate it thermally from its surroundings. Effusion cells are suitable for evaporating metals with a relatively high vapour pressure at temperatures below 1300°C to yield a growth rate of 0.1nm/s . For materials that require evaporation temperatures in excess of 1300°C it is more practical to provide the energy required for evaporation by bombarding the source directly with a high energy electron beam. In the electron beam sources the material is held in a condensed phase in a water-cooled copper hearth. The electron beam is deflected onto the material by a combination of permanent magnets and electromagnets through a trajectory of $\sim 270^{\circ}$. This arrangement enables maximum screening of the substrate from the filament, and of the filament from ions generated at the source. The beam is swept over the hearth during growth to maximise the molten region and to even out the depletion region. A feedback loop incorporating a quadrupole-flux monitor keeps the deposition rate constant throughout growth.

The rate monitor is a quartz crystal that can be placed exactly in the substrate position for accurate calibration of the fluxes. It measures the piezoelectric resonant frequency of the quartz as a function of the damping that is provided by the mass deposited on its surface. From this measurement it is possible to deduce the total thickness deposited in a set time, and hence the flux. An ultraclean environment is essential for depositing high purity rare earth films, therefore the typical background pressure during the rare earth evaporation is 4×10^{-8} mbar. This is necessary to minimise the inclusion of contaminants in the films and also the scattering processes that would degrade the flux. The growth chamber

is pumped by a turbomolecular pump and a titanium sublimation pump (TSP), both located at substrate level. Additional trapping of impurities is provided by a liquid nitrogen cryoshield that surrounds the sources. The chamber also contains in-situ monitoring and characterisation tools: a quadrupole mass spectrometer analyses the residual gas components and a reflection high energy electron diffraction (RHEED) facility provides real-time characterisation of the growth interface.

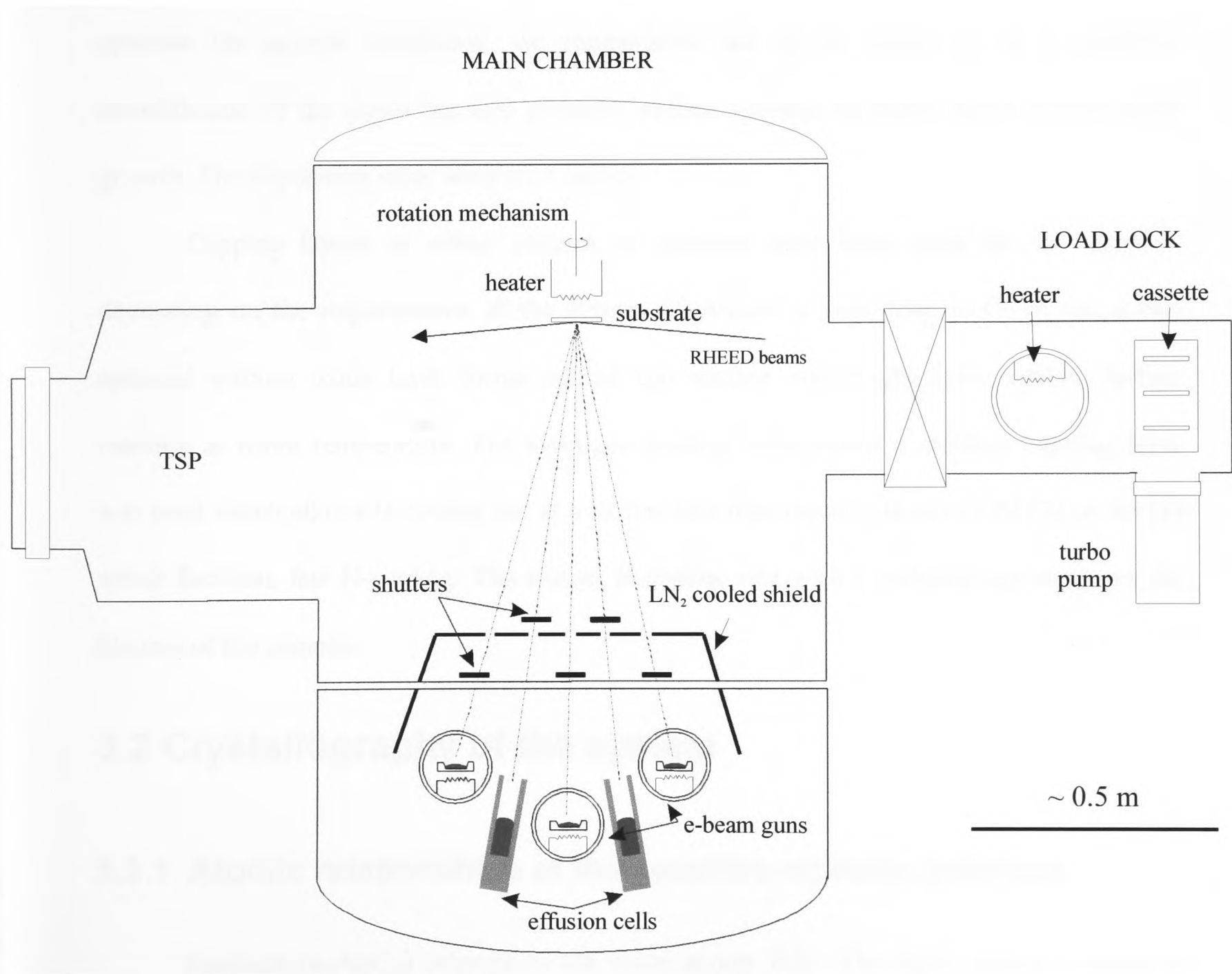


Figure 3.2: Diagram of the MBE growth chamber

3.1.2 Experimental Conditions

For this work sapphire substrates with an epitaxially polished $(11\bar{2}0)\pm 0.5^\circ$ surface were used. The substrates were solvent cleaned and annealed under UHV at approximately 750°C in the growth chamber immediately prior to deposition. The Nb and Y were evaporated from electron beam sources and the Ho was evaporated from an effusion cell. The temperature of the substrate was normally held at 750°C for deposition of the Nb buffer and at 500°C for the deposition of rare earth thin films. The temperature could be changed to optimise the growth conditions: the temperature has to be chosen so as to minimise interdiffusion of the layers but also promote surface mobility to enable good layer-by-layer growth. The deposition rates were 0.05 nm/s .

Capping layers of either yttrium or niobium have been used on the samples, depending on the requirements of the system. If yttrium is used then in O_2 or air, a thin epitaxial yttrium oxide layer forms on the top surface which effectively inhibits further reaction at room temperature. For hydrogen loading experiments a niobium capping layer was used which allows H-cycling but at a slower rate than capping layers of Pd [2] or Au [3] which facilitate fast H-cycling. The slower H-cycling rate with a niobium cap increases the lifetime of the samples.

3.2 Crystallography of the system

3.2.1 Atomic relationships at the sapphire-niobium interface

Sapphire ($\alpha\text{-Al}_2\text{O}_3$) belongs to the space group $R\bar{3}c$. The Al_2O_3 lattice consists of alternate Al and O planes perpendicular to the $[11\bar{2}0]$ direction. The Al layers are flat, with each third atomic position, in the $[0001]$ direction, lying vacant, as shown in Figure 3.3(a).

The repeat distance along $[\bar{1}100]$ is three atomic rows. There is a displacement of half the 3-row repeat distance along $[\bar{1}100]$ for the Al planes above and below. The vacancies in the Al sublattice align along the $[\bar{2}201]$ direction. The oxygen planes are similar to the Al planes, except that every atomic position is filled, and the rows of atoms parallel to the $[\bar{1}100]$ direction are corrugated rather than flat. A comprehensive report on the crystallography of sapphire is given by Lee and Lagerlof (1985) [4].

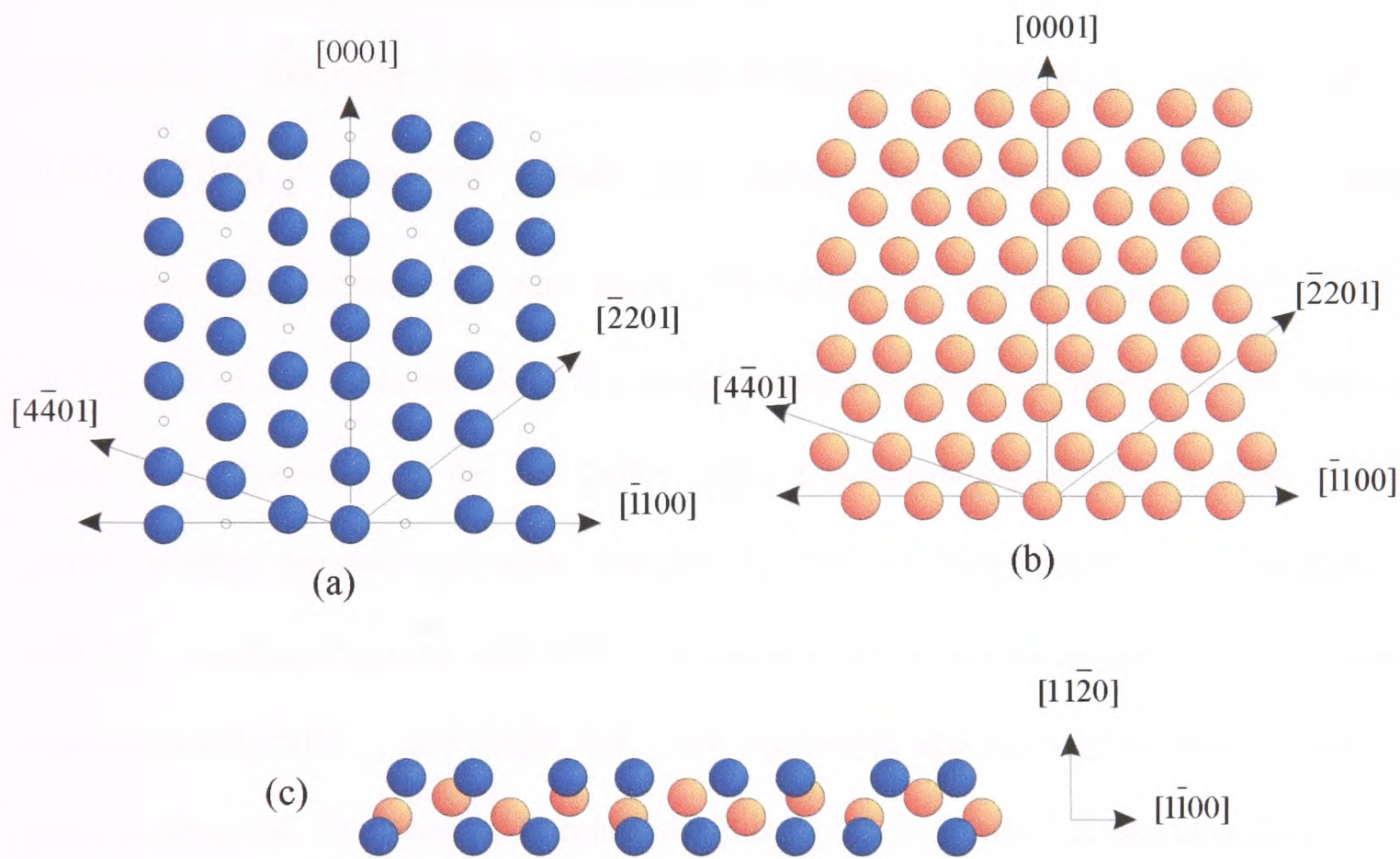


Figure 3.3: the Al_2O_3 lattice (a) $(11\bar{2}0)$ plane showing Al positions, (b) $(11\bar{2}0)$ plane showing O positions, and (c) projection along $[0001]$ direction showing corrugation of O planes

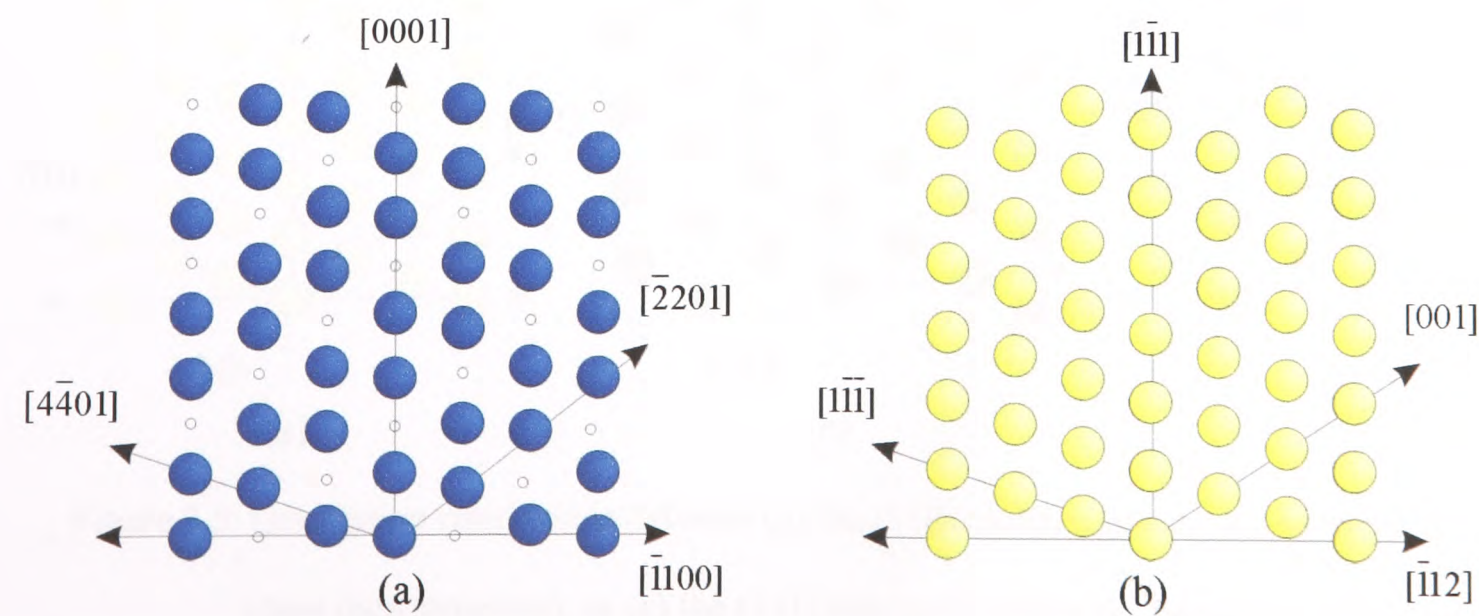


Figure 3.4: Orientation relationship between (a) the $(11\bar{2}0)$ Al_2O_3 plane and (b) the (110) niobium plane

Niobium is a body-centred cubic material. At the $(110)_{\text{Nb}} \parallel (1\bar{1}20)_{\text{sapphire}}$ interface the 3-fold axes in the two structures (bcc Nb and trigonal Al_2O_3) are aligned in the plane of the interface, i.e. $[\bar{1}\bar{1}1]_{\text{Nb}} \parallel [0001]_{\text{Al}_2\text{O}_3}$, and an untwinned Nb layer forms with $[\bar{1}\bar{1}2]_{\text{Nb}} \parallel [\bar{1}\bar{1}00]_{\text{Al}_2\text{O}_3}$. Figure 3.4 shows the orientation relationship between sapphire and Nb.

3.2.2 Atomic relationships at the niobium-rare earth interface

The $(0001)_{\text{RE}}$ plane of the hcp metal grows epitaxially on $(110)_{\text{Nb}}$ with the epitaxial relationship following the Nishiyama-Wasserman orientation such that the $[10\bar{1}0]_{\text{RE}} \parallel [\bar{1}\bar{1}0]_{\text{Nb}}$ axes are parallel [1]. Along this direction there is a supercell commensuration between the rare earth $(10\bar{1}0)$ planes (0.310 nm) and the Nb $(\bar{1}\bar{1}0)$ planes (0.234 nm) of 3:4. Although there is a unique orientation relationship of the rare earth metal when it is deposited on the Nb buffer, upon transformation to the β -phase rare earth dihydride there are two equivalent orientations, with the close packed planes changing from ABAB... stacking (hcp) to ABCABC... stacking (fcc). In the fcc structure the two stacking sequences ABCABC... and CABABC... are equivalent, and so twinning about the (111) fcc plane is observed. The orientation relationship is shown in Figure 3.5, and appendix 1.

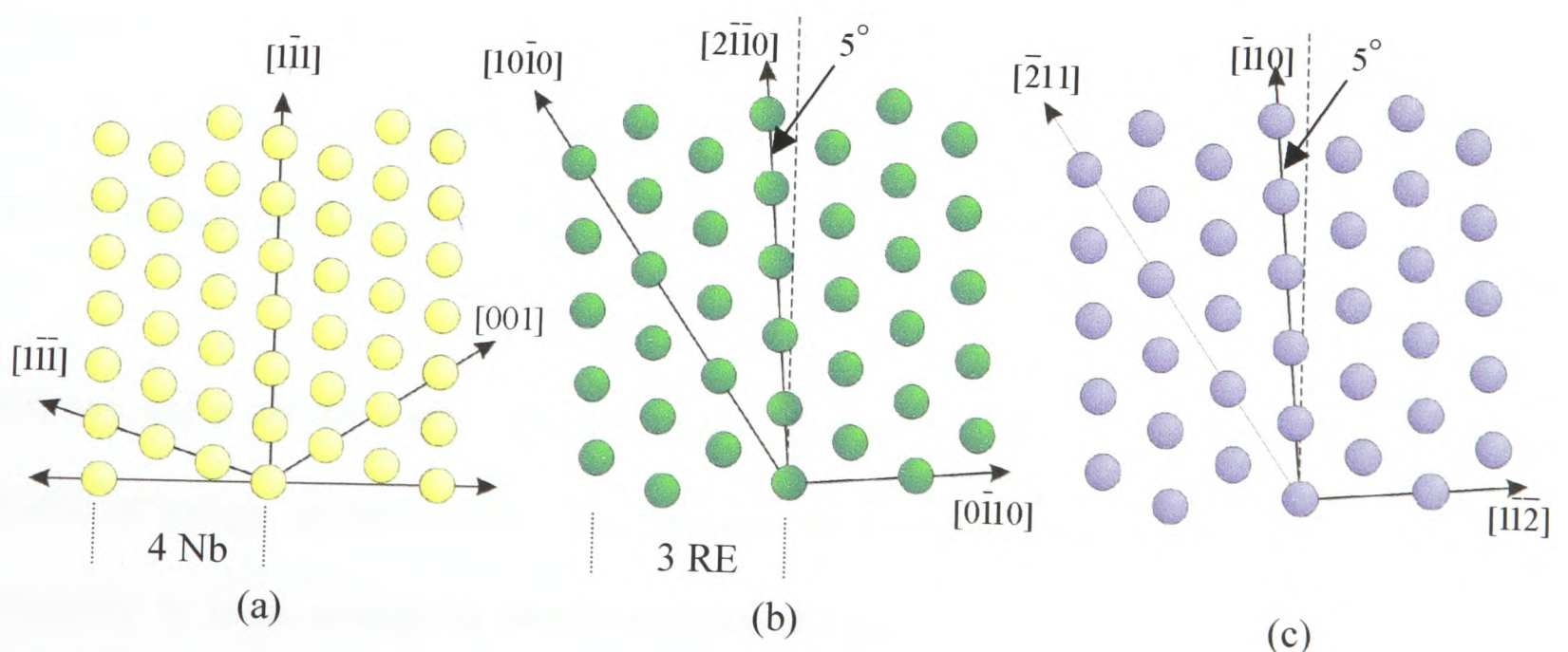


Figure 3.5: Orientation relationship between (a) the (110) niobium plane and (b) the (0001) rare earth plane (hcp structure), or (c) the (111) rare earth dihydride plane (fcc structure)

3.3 Factors affecting growth morphology

The epitaxial growth of single crystal films offers the opportunity to create synthetic structures with novel physical and chemical properties. However, for most applications of such structures smooth epilayers and atomically flat interfaces are required and so an understanding of the strain relief mechanism (usually either introduction of defects such as dislocations, or by surface roughening) and its influence on film morphology is of primary importance. To achieve this it is necessary to find a suitable substrate system on which it is geometrically possible for the superlattice structure to grow, i.e. such that there is only a small lattice mismatch between substrate and deposited material. After choosing a system that is geometrically suited for growth it is then necessary to consider both the thermodynamic constraints upon the system, and the methods of compensating for the mismatch between crystals.

3.3.1 Thermodynamic treatment of epitaxy

There are thermodynamic constraints upon a growing system that dictate whether or not it will grow with good crystalline order and with flat interfaces. Near equilibrium thin crystalline films grow by one of three mechanisms [5]. A film can grow monolayer-by-monolayer, which is known as Frank-van der Merwe (FM) or 2-D growth. The film forms by a sequence of stable uniform atomic layers with increasing coverage. Thermodynamically FM growth occurs when

$$\gamma_f + \gamma_i - \gamma_s < 0 \quad (3.1)$$

where γ_s and γ_f are the surface energies of the substrate and film respectively, and γ_i is the interfacial energy. In heteroepitaxy the condition for FM growth is that $\gamma_f < \gamma_s$ and that this inequality is large enough to satisfy equation 3.1 as in general γ_i is positive and non-negligible.

An intermediate growth mode is described as Stranski-Krastanov growth. In this case the film initially deposits layer-by-layer until after a certain thickness has been deposited, sometimes as little as one monolayer, after which this is no longer possible and 3D islands are then deposited. The thermodynamic conditions for observing SK growth are

$$\begin{aligned} (\gamma_f + \gamma_i - \gamma_s)_n &\leq 0 \quad \text{for} \quad n < n^* \\ &> 0 \quad \text{for} \quad n \geq n^* \end{aligned} \quad (3.2)$$

where n is the number of monolayers deposited and n^* is the thickness above which it is no longer possible to sustain uniform layer growth. The third growth mode is Volmer-Weber growth, where upon contact with the substrate the material immediately nucleates in 3-dimensional islands and the substrate surface may remain partially exposed until a large amount of material has been deposited. This is because the adatom interaction is so much stronger than the substrate-film interaction. Thermodynamically the condition for VW growth is

$$\gamma_f + \gamma_i - \gamma_s > 0. \quad (3.3)$$

3.3.1.1 Extension of thermodynamic treatment to include strain

This treatment can be extended to a thermodynamic treatment that includes the strain within the system; for FM growth equation 3.1 becomes [6]

$$\gamma_{fn} + \gamma_{in} - \gamma_s < 0 \text{ for all } n \text{ (i.e. independent of thickness)}. \quad (3.4)$$

The n -dependent strain energy (which is a function of n – the number of layers deposited) has been absorbed into γ_{in} , which is now the strain dependent interfacial energy. γ_{fn} (surface energy of the film, now including strain) deviates from γ_f due to the n -dependent surface strain. This condition is rigorously fulfilled for homoepitaxial growth where $\gamma_f = \gamma_s$ and $\gamma_{in} = 0$. Another ideal fulfilment of this condition is for the case of zero misfit, where the condition becomes

$$\gamma_{\text{fm}} + \gamma_{\text{in}}^0 - \gamma_{\text{s}} < 0 \quad (3.5)$$

where γ_{in}^0 is the zero contribution to the strain energy which then depends on the specific chemical interaction between the film and the substrate atoms and it rapidly approaches zero within the first few monolayers. In all other cases, however, the strain energy increases with n , and therefore γ_{in} increases until at a given $n=n^*$ the FM condition is no longer fulfilled, and 3D crystals begin to form (SK mode).

For superlattice growth FM is desired, and it occurs only under the condition that

(i) $\gamma_{\text{f}} < \gamma_{\text{s}}$, and

(ii) γ_{in} is small

Obviously condition (i) cannot be fulfilled both for the growth of B on A (in a superlattice of layers ABAB...) and for the growth of A on B. The ideal condition can be approached for $\gamma_{\text{A}} \approx \gamma_{\text{B}}$ and small γ_{in} . If γ_{A} and γ_{B} differ widely then the metal with larger γ will form 3D clusters and suppress the superlattice growth. This can be overcome in part by increasing the growth rate or decreasing the substrate temperature. This takes the system further away from equilibrium conditions and acts to enhance the nucleation rate of the 3D crystals so that the nucleation rate becomes so large that clusters merge into a continuous multilayer before the desired thickness is reached.

In superlattice growth, true FM growth is not achievable and there will be a certain roughness between the layers. However the interface energy acts to minimise the interface area and if the experimental conditions are chosen such that rearrangements on an atomic scale can occur during the interface formation then the interface will become smoother and it is possible to grow superlattices of sufficient quality and thickness for x-ray and neutron diffraction experiments.

3.3.2 Strain and critical thickness

3.3.2.1 Coherent, semicoherent and incoherent interfaces

Even when the best geometric fit between two crystals is found, the planes will at best only fit approximately. The mismatch can be compensated for in one of three ways. In a coherent interface the lattice mismatch between substrate and metallic overlayer is accommodated entirely by straining the metal layer. Such interfaces are periodic parallel to the interface. A coherent interface is shown in Figure 3.6 (a). The other extreme is an incoherent interface which forms between two rigidly connected lattices. There is no periodicity parallel to the interface. An incoherent interface is shown in Figure 3.6 (c). An interface can also be semicoherent (Figure 3.6 (b)). In a semicoherent interface misfit dislocations separate coherent regions. The dislocations either accommodate the lattice mismatch partially, thus leaving the film with strain, or completely, where the lattice of the film is not strained. Figure 3.7 shows schematically how the introduction of misfit dislocations relieves the strain in a semicoherent system. In this model the upper crystal can be thought to have stretched in the c -direction to give a perfect fit at the interface, then parallel edge dislocations are introduced which have the effect of reducing the strain at large distances. The number of extra planes to be accommodated in the upper crystal is

$$\rho = \frac{1}{a_1} - \frac{1}{a_2} \quad (3.6)$$

and the dislocation spacing $p = \rho^{-1}$ is given by

$$p = \frac{a_1 a_2}{a_2 - a_1} \quad (3.7)$$

The dislocations result in a distortion of the lattice perpendicular to the interface plane. In order to understand how dislocations interact with each other and with other lattice defects it is necessary to understand the distortion of the crystal structure around a

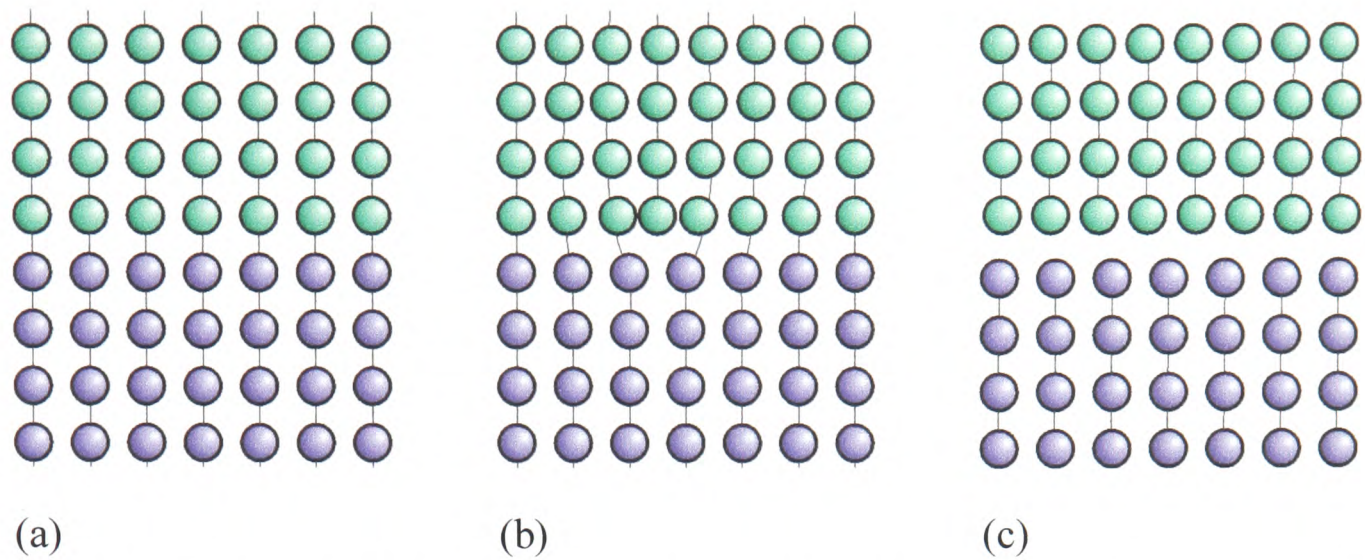


Figure 3.6: Schematic diagram of (a) a coherent, (b) a semicoherent and (c) an incoherent interface

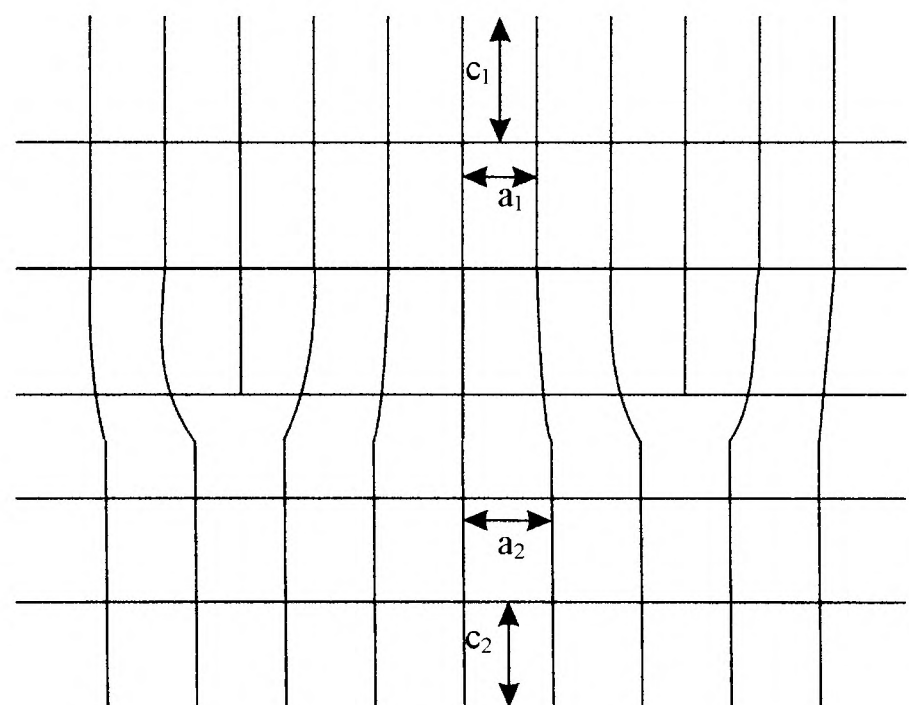


Figure 3.7: interface between two crystals, the interface is normal to the plane of the figure

dislocation. The simplest approach is to consider an elastic continuum containing a dislocation. However this approach is not valid close to the dislocation as the strain is very large. It is therefore usual to define a region around a dislocation, known as the dislocation core, with radius of $r \sim 5D$ (D is the total displacement due to the dislocation) which effectively marks the boundary of the elastic body. Calculation of the atomic displacements within this core requires a detailed knowledge of the forces acting on the system, but outside this core it remains valid to treat the crystal as an elastic continuum.

3.3.2.2 Critical thickness

For MBE growth of crystals with differing lattice parameters, pseudomorphic growth, i.e. when the growing layer is strained to match the substrate such that a perfectly matched epilayer is formed, is possible below a critical thickness. Above this critical thickness it is energetically favourable for some, or all, of the layer strain to be relaxed by the introduction of misfit dislocations. There are two separate approaches to the idea of critical thickness, a geometrical approach [7] or a consideration of the strain energy in the layer, the strain energy of a dislocation and the mechanisms whereby misfit dislocations can be generated [8,9]. All the models agree with experiment to within a factor of about 2 and the key result of all models is that the critical thickness is inversely proportional to the strain. The independent success of these models (i.e. those considering only the geometry and those considering only the energy of the systems) implies that neither approach is wholly correct or sufficient to predict the critical thickness. The following sections will consider both approaches to predict the critical thickness for the rare earth systems and consider how widely they are applicable.

3.3.2.3 Geometrical approach

Within the superlattice systems, it is the rare earth (0001) / rare earth (0001) interfaces that are closest to the ideal model system, and so this interface is used to illustrate the simple geometrical approach of Dunstan *et al.* [7]. This approach enables the prediction of the strain and of the thickness at which it becomes energetically favourable for misfit dislocations to form. The interface to be considered is shown in Figure 3.8.

The substrate and the film have bulk hexagonal lattice parameters a_s , c_s and a_f , c_f respectively. For the simple case of a coherent interface the strained layer will distort such that the in-plane lattice parameters of the film become equal to those of the substrate and there will be an out-of-plane contraction for $a_f < a_s$ and an expansion for $a_f > a_s$.

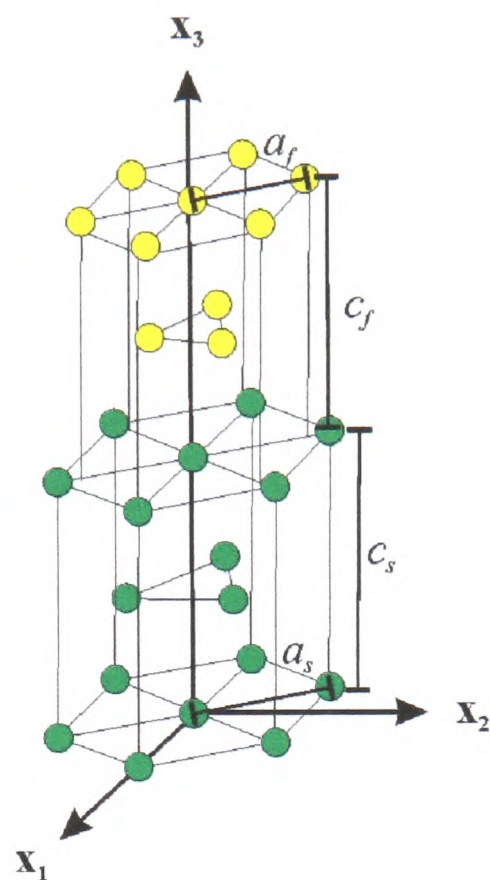


Figure 3.8: strained epitaxial layer in the (0001) orientation

The distortion results in forces acting within the crystal system, with the force per unit area described as the stress. The general homogeneous stress components (i.e. the forces acting on an element of fixed shape and orientation which are independent of the position of the element in the body) are given by

$\sigma_{11}, \sigma_{21}, \sigma_{31}$

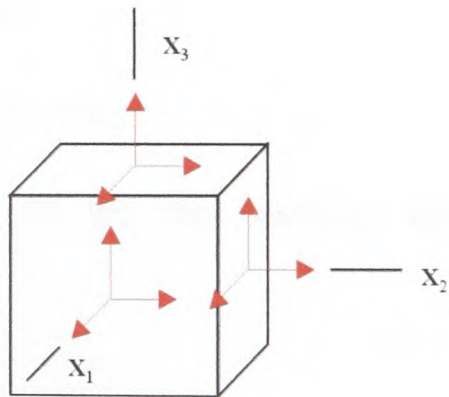
$\sigma_{12}, \sigma_{22}, \sigma_{32}$

$\sigma_{13}, \sigma_{23}, \sigma_{33}$

at x_1

at x_2

at x_3



and the generalised stress tensor is

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix}$$

which when referred to the principal axes in the Cartesian system reduces to

$$\begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{pmatrix}.$$

The strain within the system, i.e. the variation of displacement u_i with position x_i , defines the tensor components

$$e_{ij} = \frac{\partial u_i}{\partial x_j} \quad (i, j = 1, 2, 3) \quad (3.8)$$

where e_{11} , e_{22} , e_{33} are the extensions along x_1 , x_2 and x_3 and e_{12} is the rotation about x_3 towards x_1 of a line element parallel to x_2 . The strain tensor is defined as the symmetrical part of $[e_{ij}]$

$$\varepsilon_{ij} = \frac{1}{2} (e_{ij} + e_{ji}). \quad (3.9)$$

For homogeneous 3D strain all the e_{ij} components are constant, and referred to the principal axes the strain is

$$\varepsilon_{ij} = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}. \quad (3.10)$$

for the case of bisotropic strain, i.e. the strain is isotropic in the plane of the interface, such as is the case for the hexagonal (0001) interface, then

$$\varepsilon_1 = \varepsilon_2 = \varepsilon_{\parallel} \quad \varepsilon_3 = \varepsilon_{\perp} \quad (3.11)$$

From the requirement that σ_3 is zero, because of the free surface, the stress-strain relationship can be simplified,

$$\sigma_i = \begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \varepsilon_i = \begin{pmatrix} \varepsilon_{\parallel} & 0 & 0 \\ 0 & \varepsilon_{\parallel} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix}. \quad (3.12)$$

Hooke's law states that the stress at any point is linearly related to the strain provided that the strain is very small. The stress-strain relationship is given by

$$\sigma_i = c_{ij} \varepsilon_j \quad (3.13)$$

where c_{ij} are the components of the stiffness tensor, and for the hexagonal case these can be derived to be [10]

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2(c_{11} - c_{12}) \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (3.14)$$

From this it can be seen that

$$\sigma_{11} = c_{11} \varepsilon_{||} + c_{12} \varepsilon_{||} + c_{13} \varepsilon_{\perp} \quad (3.15)$$

$$\sigma_{33} = c_{13} \varepsilon_{||} + c_{13} \varepsilon_{||} + c_{33} \varepsilon_{\perp} \quad (3.16)$$

therefore

$$\varepsilon_{\perp} = -2(c_{13}/c_{33}) \varepsilon_{||} \quad (3.17)$$

and

$$\sigma_1 = \varepsilon_{||} (c_{11} + c_{12} - 2c_{13}^2 / c_{33}) = M \varepsilon_{||} \quad (3.18)$$

where M is a 2-D Young's modulus.

The elastic energy density, u , of the layer can be expressed in terms of the stress and strain tensors as

$$u = \frac{1}{2} \sum_i \sigma_i \varepsilon_i = \frac{1}{2} (\sigma_1 \varepsilon_1 + \sigma_2 \varepsilon_2) \quad (3.19)$$

$$= \frac{1}{2} (\sigma_1 \varepsilon_{||} + \sigma_1 \varepsilon_{||}) \quad (3.20)$$

substituting from equation 3.18;

$$= M \varepsilon_{||}^2 \quad (3.21)$$

The elastic energy, U , of a layer of thickness h can be written as

$$U = hu \quad (3.22)$$

$$U = hM\varepsilon_{\parallel}^2. \quad (3.23)$$

Thus the elastic energy depends on the square of the misfit.

The introduction of dislocations lowers the elastic strain energy as the strain is relieved, however the dislocations possess a self-energy and for an array of dislocations spaced a distance p apart, the energy per unit area of the interface due to the dislocations, E_{dis} , for an isotropic medium is given by [11]:

$$E_{dis} = \frac{Gb^2}{4\pi(1-\nu)} \frac{1}{p} \ln\left(\frac{\beta h}{b}\right) \quad (3.24)$$

where β is a constant, ν is Poisson's ratio, G is the shear modulus and b is the magnitude of the Burgers vector. Thus the elastic strain increases as $h\varepsilon_{\parallel}^2$, while the energy of the dislocations increases linearly with strain, as p is inversely proportional to the strain, as can be seen from equation 3.7. Therefore by considering the energy of the system a simple prediction can be made such that below the critical thickness h_c the pseudomorphic layer is dislocation free but above a certain thickness it is energetically favourable to introduce dislocations to relieve the strain.

From the model of bisotropic strain it is hard to make an estimate of the critical thickness because the strain is different in the directions parallel or perpendicular to the plane of the interface. However, if the material is assumed to be isotropic, i.e. the strain is equal in all directions, then a simple argument can be used to estimate the critical thickness: for an isotropic material the strain field of a dislocation at a depth h from the surface must decay laterally to zero within approximately h , so a dislocation can only relieve strain over a lateral distance mh where $m = 1, 2$. Outside this region the relaxation is zero, and inside the average relaxation is of order b/mh . A dislocation cannot be produced when b/mh is larger

than the strain in the layer. Therefore at small thicknesses the layer is prevented from relaxing as $b/mh > \varepsilon_0$, where ε_0 is the isotropic strain. The strain is able to relax when

$$\frac{b}{mh} = \varepsilon_0 \quad (3.25)$$

which gives a critical thickness of

$$h_c = \frac{b}{m\varepsilon_0} \quad (3.26)$$

if b is of the same order as the atomic separation and $m=1$, then the critical thickness in units of monolayers is given by;

$$h_c = \frac{1}{\varepsilon_0} \quad (3.27)$$

However when the production of misfit dislocations is inhibited (e.g. the common Burgers vector and their glide directions for a given crystal system may not always be efficient at relieving the strain at certain oriented interfaces) it can be possible to grow strained layers much thicker than the critical thickness.

3.3.2.4 Matthews and Blakeslee theory of critical thickness

This geometrical approach is a simple calculation, only valid for the case of isotropic strain between two crystals. More sophisticated treatments of the case of a monolayer on a substrate have been reported by Frank and van der Merwe [8] and this work was extended by Matthews and Blakeslee [9] to be relevant for the case of epitaxial multilayers. They used a method which considers the forces on dislocation lines in the interface. Two of the most important forces are the force exerted by the strained layer on a section of dislocation threading through it, $F_{\varepsilon_{\max}}$, and the tension in the dislocation line, F_l .

When

$$F_{\varepsilon_{\max}} < 2F_l \quad (3.28)$$

the interface is coherent, because it costs too much energy to extend the dislocation line, and the geometry of the dislocation is shown as line (a) in Figure 3.9.

When

$$F_{\varepsilon_{\max}} > 2F_l \quad (3.29)$$

then the dislocations can move and the strain energy will be relieved by the creation of misfit dislocations, as shown by line (c) in Figure 3.9. Thus the critical thickness is given by the value of the thickness when $F_{\varepsilon_{\max}} = 2F_l$ (line (b) Figure 3.9).

The critical thickness when these two forces are balanced is shown to be [9]

$$h_c = \frac{b}{2\pi f} \frac{(1 - \nu \cos^2 \alpha)}{(1 + \nu) \cos \lambda} \left(\ln \frac{h_c}{b} + 1 \right) \quad (3.30)$$

where α is the angle between the dislocation line and its Burgers vector, λ is the angle between the slip direction and the direction in the film plane which is perpendicular to the line of intersection of the slip plane and the interface, f is the lattice mismatch, b the magnitude of the Burgers vector and ν is the Poisson ratio.

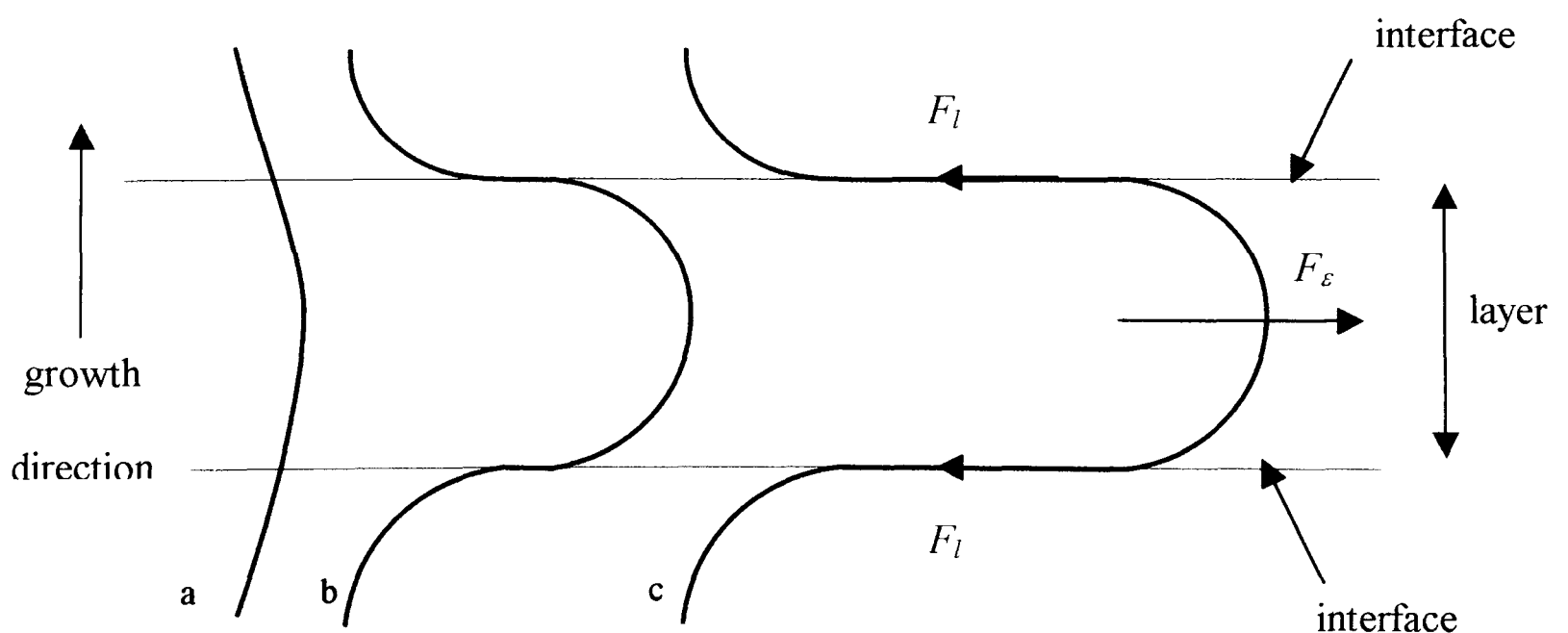


Figure 3.9: threading dislocations in (a) coherent (b) critically thick and (b) incoherent multilayers

3.3.2.4 Extension of the Matthews and Blakeslee theory to account for regions of high strain

The Matthews and Blakeslee theory breaks down at high strains (i.e. small h_c), because it ignores the fact that at high strains the stress field of one dislocation will affect the adjacent dislocation. When two dislocations are sufficiently close to one another then it is no longer valid to regard them as isolated, and in fact the joint contribution to the total energy of two interacting dislocations is different to that of two non-interacting dislocations. Downes *et al.* modified equation 3.30 to make it applicable for systems containing high strains by using the model system where relaxation is assumed to occur by the introduction of pure edge dislocations, i.e. $\alpha=90^\circ$, and $\lambda=0^\circ$ in equation 3.30. This gives an expression for the critical thickness as [12]

$$h_c = \frac{b}{4\pi(1+\nu)\varepsilon} \ln \left| \frac{h_c}{b} + 1 \right|. \quad (3.31)$$

For comparison between equations 3.30 and 3.31, if a film is strained so that the lattices of the film and substrate are at register at the interface, then $\varepsilon=f$. If the misfit is shared between dislocations and strain, then

$$f = \varepsilon + \delta \quad (3.32)$$

where δ is the misfit accommodated by dislocations.

3.3.2.5 Relaxation above the critical thickness

Although there are several models for predicting the critical thickness, relatively little work has been done on the way in which layers relax above the critical thickness, and it is not clear whether the strain relaxes smoothly with increasing thickness above the critical thickness, or discontinuously at the critical thickness. Dunstan *et al.* [7] have developed a geometrical model of the plastic relaxation of strained layers, by refining the

model described in section 3.3.2.3. In the model, dislocations with an associated strain field of width md (m – integer, d – dislocation core size) may form anywhere independently at the interface. However there will be random gaps between the dislocations, whose width cannot be greater than md or another dislocation would form. Statistically the average gap is $\frac{1}{3} md$, and so $\frac{3}{4}$ of the initial strain is relieved. Subsequent to the formation of misfit dislocations we can consider the semicoherent interface to be identical to a coherent interface with the overlayer having a strain of $\epsilon/4$. Equation 3.24 then predicts a new critical thickness four times as large, and so the strain would be relieved in a stepwise fashion, with the strain reducing by a factor of 4 as the layer thickness increases by the same factor, as shown by the red line (ii) in Figure 3.10. Alternatively, the actual size of the gaps

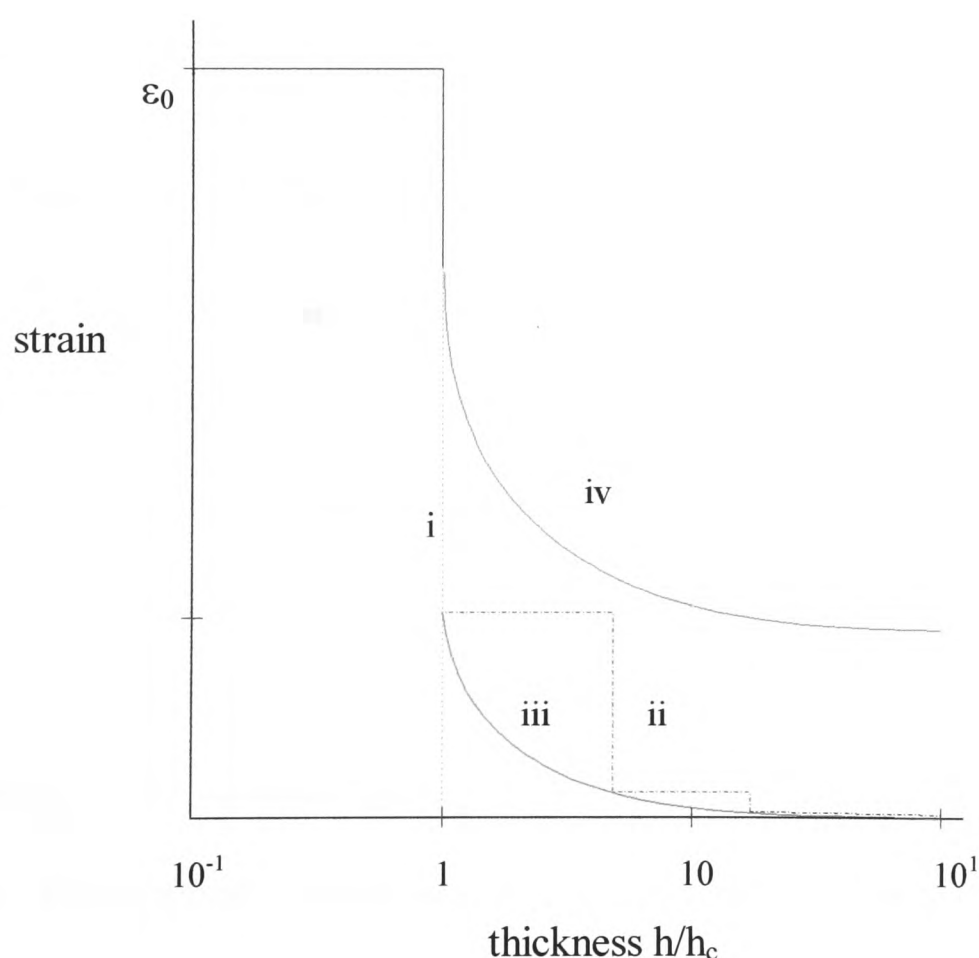


Figure 3.10: Relaxation as a function of thickness (i) discontinuous complete relaxation predicted by idealised models. (ii) stepwise relaxation of a layer where the interface is identical before and after introduction of misfit dislocations, only the strain state is changed (iii) smoothing effect due to random gap size (iv) effect of residual strain surrounding a dislocation core on initial relaxation

between dislocations can also be considered. The gaps are not of uniform width, and as the larger gaps will tend to induce further relaxation before the narrow gaps, this will act to smooth the steps between the thicknesses at which misfit dislocations form, shown by the green line (iii) in Figure 3.10. A further improvement to the model is to realise that outside the dislocation core there is not in fact a physical barrier. Thus although inside the core the relaxation is zero, outside the core the relaxation falls away exponentially over a characteristic length of approximately d outside the dislocation region md . This discourages the formation of other dislocations within a region of length $2md$ or more from the dislocation. This does not affect the critical thickness calculation, but reduces the initial number of dislocations by a factor of 2. So although statistically in the idealised model three-quarters complete relaxation is expected, this refinement shows that only a third or less of the initial strain will be relieved, as is shown by the blue line (iv) in Figure 3.10.

3.3.2.6 Relevance of the critical thickness theories to rare earth epitaxy

The initial growth in the system is the heteroepitaxial growth of niobium on sapphire, i.e. when the difference of the chemical potential of the substrate and of the film is due mainly to the difference in strength of the chemical bonds irrespective of the value of the lattice misfit. It is assumed that ionic bonds dominate at the interface [13] due to the need to establish charge neutrality at the surface. The crystal structures of the two crystals are different, with niobium having a bcc structure and sapphire having a rhombohedral structure. The epitaxial growth is achieved between niobium and sapphire by a geometrical fit between particular rows of atoms in the two crystals. Such an interface is therefore extremely complicated and the application of simple strain relief theories are likely to be of limited use, as such models do not account for the difference in bonding or the lattice structure of the misfit.

The growth of rare earth on niobium is again heteroepitaxial, with the bonding of both materials being metallic, but the lattices of the two structures are quite different (bcc and hexagonal close packed). The strain within the niobium is not isotropic or even bisotropic, but is different along each of the principle axes. However the first rare earth layer (Y) is deposited as a seed layer and is grown until its thickness is sufficiently above the critical thickness such that it has completely relaxed to its bulk lattice parameters. The subsequent growth of the superlattice is thus unaffected by any strain remaining in the substrate system.

The rare earth/rare earth interface is much closer to the model systems discussed as it involves similar materials, where the lattice across the interface is single structure, the bonding metallic and there is only a small difference in lattice parameters. The stress within this system is bisotropic and the simple theories of Dunstan and Downes will be applicable.

References

- [1] J. Kwo, M. Hong, and S. Nakahara, *Appl. Phys. Lett.* **49**, 319 (1986).
- [2] J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, *Nature* **380**, 231 (1996).
- [3] A. R. Wildes, R. C. C. Ward, M. R. Wells, and B. Hjörvarsson, *J. Alloys and Compounds* **242**, 49 (1996).
- [4] W. E. Lee and K. P. D. Lagerlof, *Journal of Electron Microscopy* **2**, 247 (1985).
- [5] E. Bauer, *Z. Krystallogr.* **110**, 372 (1958).
- [6] E. Bauer and J. H. van der Merwe, *Phys. Rev. B* **33**, 3657 (1986).
- [7] D. J. Dunstan, S. Young, and R. H. Dixon, *Appl. Phys.* **70**, 3038 (1991).
- [8] F. C. Frank and J. H. van der Merwe, (1949).
- [9] J. W. Matthews and A. E. Blakeslee, *J. Cryst. Growth* **27**, 118 (1974).
- [10] J. F. Nye, *Physical Properties of Crystals*, 2 ed., Oxford University Press, Oxford, (1995).

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- [11] A. Kelly, G. W. Groves, and P. Kidd, *Crystallography and Crystal Defects*, Revised ed., John Wiley & Sons Ltd., Chichester, (2000).
- [12] J. R. Downes, D. J. Dunstan, and D. A. Faux, *Phil. Mag. lett.* **76**, 77 (1997).
- [13] G. Gutekunst, J. Mayer, and M. Ruhle, *Phil. Mag. A* **75**, 1329 (1997).

Chapter 4

Characterisation Techniques

This chapter explains the characterisation techniques used in this thesis, with the main part of the chapter concentrating on electron diffraction techniques, as the majority of the samples were characterised initially with both reflection high energy electron diffraction, RHEED, and high resolution electron microscopy, HREM, techniques. Section 4.1 explains the theory of electron diffraction, with section 4.2 using the principles of electron diffraction to explain the techniques of high resolution electron microscopy and RHEED. Section 4.3 explains the experimental techniques used to make specimens suitable for use in an electron microscope. The chapter concludes with a brief discussion of other techniques employed as part of this thesis. Section 4.4 discusses the scanning probe techniques used in chapter 7 to study the hydrogen induced deformation of thin epitaxial films of holmium and section 4.5 discusses the neutron scattering techniques used to study the magnetic structure of single crystal thin films of HoD_{2+x} as presented in chapter 9.

4.1 Electron Diffraction

4.1.1 Elastic scattering of electrons by crystals

The most simple theory assumes that electrons suffer only one scattering event as they pass through a crystal, which is the ideal condition of *kinematic scattering*, and the

situation for electrons is then analogous to x-rays which are only weakly affected by atoms and are likely to suffer only one scattering event. In reality an electron beam interacts strongly with a specimen, and a beam that has been diffracted once can be rediffracted by the specimen, and so on. This is known as *dynamical scattering*.

Bragg's law is the most simple explanation of the observed angles by which electrons are diffracted from a crystal. Maxima in intensity occur when the waves diffracted by parallel planes of atoms interfere constructively. From Figure 4.1 it can be seen that this condition is satisfied when

$$2d \sin \theta = n\lambda \quad (4.1)$$

where d is the crystal plane spacing, and n denotes fractional lattice spacings.

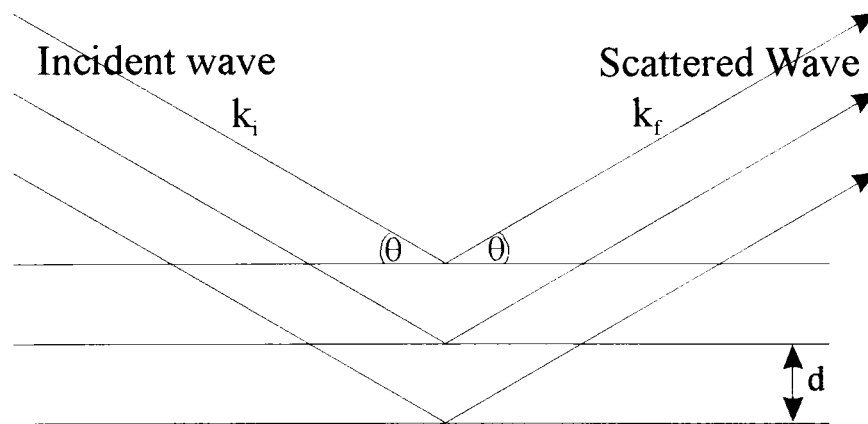


Figure 4.1 : Bragg scattering from a crystal

It is useful to use the reciprocal lattice construction to extend this simple equation, so if we consider a real unit cell with sides $\mathbf{a}, \mathbf{b}, \mathbf{c}$, with atomic positions defined by

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} \quad (4.2)$$

then the corresponding reciprocal lattice unit cell has sides $\mathbf{A}, \mathbf{B}, \mathbf{C}$ with reciprocal lattice vectors given by

$$\mathbf{g}_{hkl} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C} \quad (4.3)$$

$$\text{where } \mathbf{A} = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad \mathbf{B} = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad \mathbf{C} = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}.$$

If we consider scattering from two atoms, as shown in Figure 4.2, where $\mathbf{r}_i$ is the vector connecting two lattice sites, then the condition for diffracted beams to interfere constructively can be expressed as

$$\mathbf{r}_i \cdot (\mathbf{k}_i - \mathbf{k}_f) = n \quad (4.4)$$

with n being an integer. This expression is satisfied for the Laue condition, such that

$$\Delta \mathbf{k} = \mathbf{k}_i - \mathbf{k}_f = \mathbf{g} \quad (4.5)$$

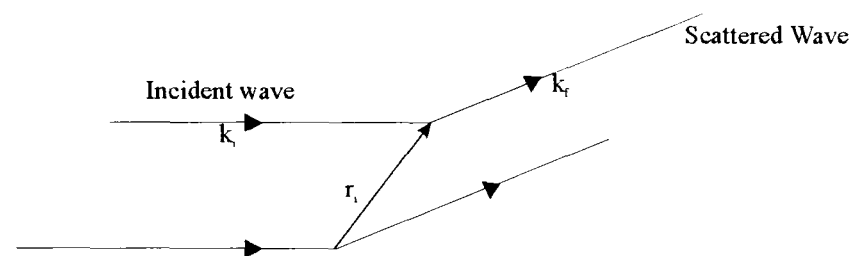


Figure 4.2 : Diffraction of a wave through a crystal

Thus the incident and scattered waves are related to each other by a reciprocal lattice vector $\mathbf{g}$ which connects the two wavevectors. This conclusion is explained graphically by the Ewald sphere construction. For the case of elastic scattering, i.e.

$$|\mathbf{k}_i| = |\mathbf{k}_f| \quad (4.6)$$

it is possible to draw a sphere from the origin, with radius $|\mathbf{k}_i|$, that defines all possible diffracted beams $\mathbf{k}_f$. From the Laue condition, it is known that only reciprocal lattice points will give reflections, so allowed reflections occur where the Ewald sphere intersects with a reciprocal lattice point. The intersection of the sphere with a reciprocal lattice point is related to the incident wavevector $\mathbf{k}_i$ by a reciprocal lattice vector $\mathbf{g}$, as shown in Figure 4.3.

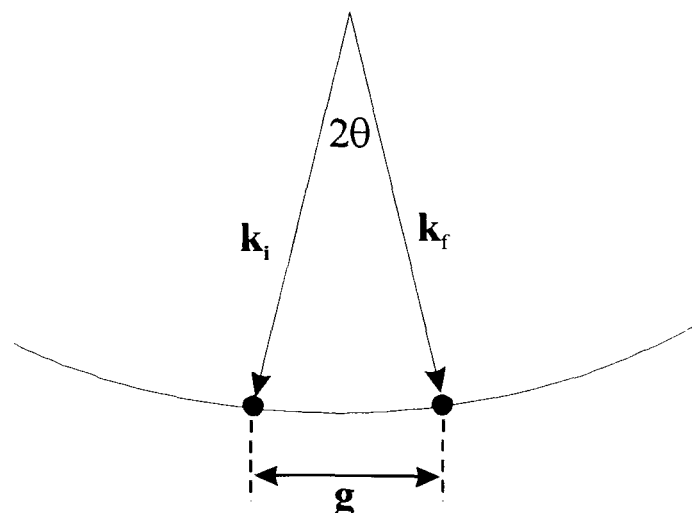


Figure 4.3: Ewald sphere construction showing relation between incident and diffracted wavevector

4.1.2 Scattering of electrons by crystals

A perfectly periodic infinitely thick crystal would produce a set of delta-function reciprocal lattice points. However, a TEM specimen is thin and so the reciprocal lattice points can be considered to be extended into rods, with a distribution in scattering power that has a sharp maximum at the reciprocal lattice point, and has a width inversely proportional to the crystal thickness. It is also interesting to note that the radius of the sphere is much greater than the separation of the reciprocal lattice points

$$\text{Radius of sphere} = \frac{2\pi}{\lambda} = \frac{\sqrt{2mE}}{\hbar} = 3.83 \times 10^{12} \text{m}^{-1} \tag{4.7}$$

where λ (400keV electrons) = 0.00164nm

$$\text{Separation of points} = \frac{2\pi}{a_0} = 1.9 \times 10^{10} \text{m}^{-1} \tag{4.8}$$

Thus the surface of the Ewald sphere appears to be quite flat cuts through several extended regions giving rise to a number of diffracted beams, as shown in Figure 4.4.

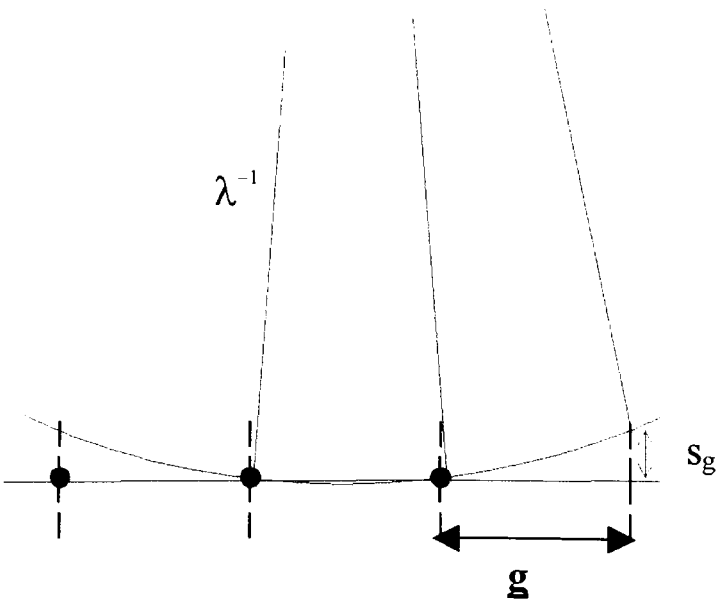


Figure 4.4 : Intersection of Ewald sphere with extended regions around reciprocal lattice points

4.1.2.1 The Structure Factor

The amount that a particle is scattered as it passes through a material is given by the scattering cross-section $d\sigma(\theta)/d\Omega$. The atomic scattering factor, $f(\theta)$, is related to the differential elastic scattering cross-section by the relation

$$|f(\theta)|^2 = \frac{d\sigma(\theta)}{d\Omega} \quad (4.9)$$

and is a measure of the amplitude of an electron wave scattered by an atom. $|f(\theta)|^2$ is proportional to the scattered intensity, where

$$f(\theta) = \frac{me^2}{2h^2} \left(\frac{\lambda}{\sin \theta} \right)^2 (Z - f_x) . \quad (4.10)$$

This accounts for the nuclear scattering of the electrons with the Z -term, and the electron charge cloud scattering in the f_x term. The f_x values used in this work are taken from the *International Tables of Crystallography* [1].

The contribution from a single atom at a position $\mathbf{r}$ is given by the atomic form factor plus a phase factor that is dependent on atom position. This scattering is given by

$$\mathbf{F} = f(\theta) e^{i\mathbf{k} \cdot \mathbf{r}} . \quad (4.11)$$

Then summing over all atoms and utilising the Laue condition we see that the structure factor $\mathbf{F}$ is given by

$$\mathbf{F} = \sum_{j=1}^n \sum_{i=1}^m f_j(g) e^{2\pi i [\mathbf{g} \cdot \mathbf{r}_i]} \quad (4.12)$$

where j sums over atom types, and i sums over atom positions.

This is completely general and can be applied to all crystal lattices. It is from this basic equation that all diffraction patterns are calculated. However it is not possible to use this equation to analyse quantitatively the intensity within a diffraction pattern to gain structural information about a system as with x-rays, as it neither accounts for dynamical scattering events, nor for the extension of the reciprocal lattice points due to the finite

nature of the specimen. If we consider a perfect specimen of uniform thickness H , then the reciprocal lattice points are elongated along the direction parallel to the foil normal. Simple diffraction theory gives the rods a scattering power of the form

$$\frac{\sin^2(\pi H s_g)}{(\pi s_g)^2} \quad (4.13)$$

where s_g is the excitation error, or the distance along C between the reciprocal lattice point and the Ewald sphere. Dynamical scattering, i.e. the fact that an electron suffers more than one scattering event as it passes through the sample means that each spot in the diffraction pattern acts as a new incident beam, and the positions of the new peaks can be inferred by adding the existing diffraction pattern at these points. A very common example of this is seen in the $[110]$ diffraction pattern from silicon. Silicon has the diamond cubic structure, and as such the (200) reflection is forbidden, but the (200) reflection is present in a $[110]$ pattern because the allowed $(11\bar{1})$ diffracted beam is rediffracted by the $(\bar{1}11)$ plane, and as $(11\bar{1}) + (\bar{1}11) = (200)$, then this beam is seen due to dynamical scattering events.

4.2 Imaging of Crystals

4.2.1 Electron Microscopy

The high resolution electron microscopy, HREM, studies were performed on a JEOL 4000EX operating at 400 keV, with a point resolution of 0.16nm. This section aims to give an overview of the main concepts of electron microscopy. There are several excellent texts which cover the subject in more detail and particular reference is made to the texts by Spence [2], Buseck, Cowley and Eyring [3] and Hirsch et al. [4].

It is possible to understand imaging with electrons by considering the analogue of the simple optical microscope. This approach is adequate, but it must be remembered that for electrons (as for light) the description is not wholly accurate or universally applicable. Figure 4.5 shows a simple geometric diagram of a microscope.

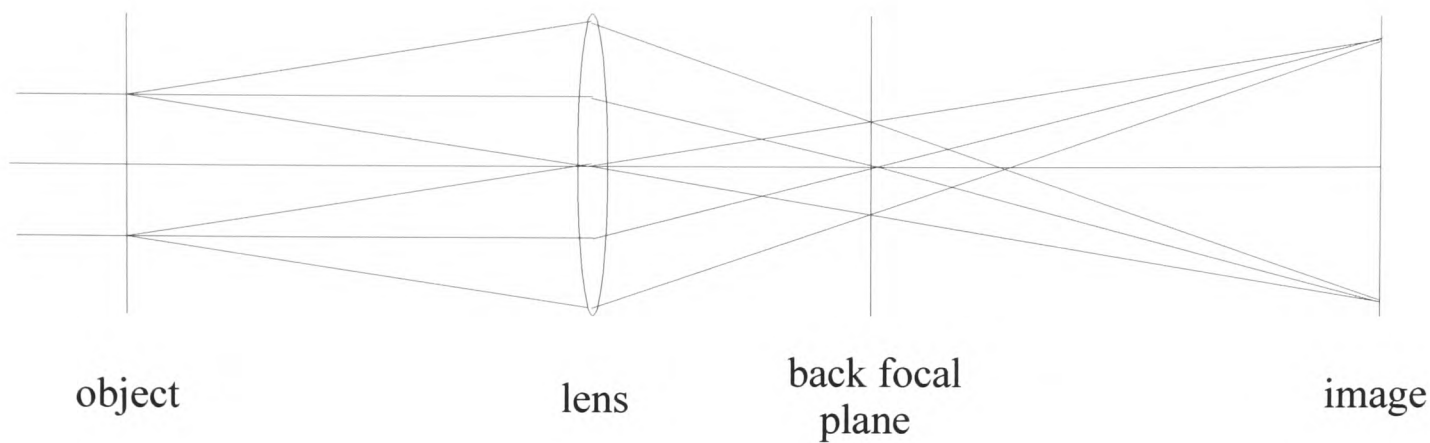


Figure 4.5 : Geometric diagram of microscope

The diffraction pattern is observed in the back focal plane, where rays scattered through an angle θ are brought together at a point, a distance $X=f \theta$ from the axis (f -focal length of lens). In this plane the Fraunhofer diffraction pattern is formed. Continuing the rays to the image plane we see that rays from a common point in the object converge on a common point in the plane. Thus the diffraction pattern in the back focal plane can be described by the Fourier transform of the wave amplitudes at the exit surface of the specimen. In the image plane we see the image of the object produced by the interference of the waves from the back focal plane. This formation can be considered from wave optics as shown in Figure 4.6.

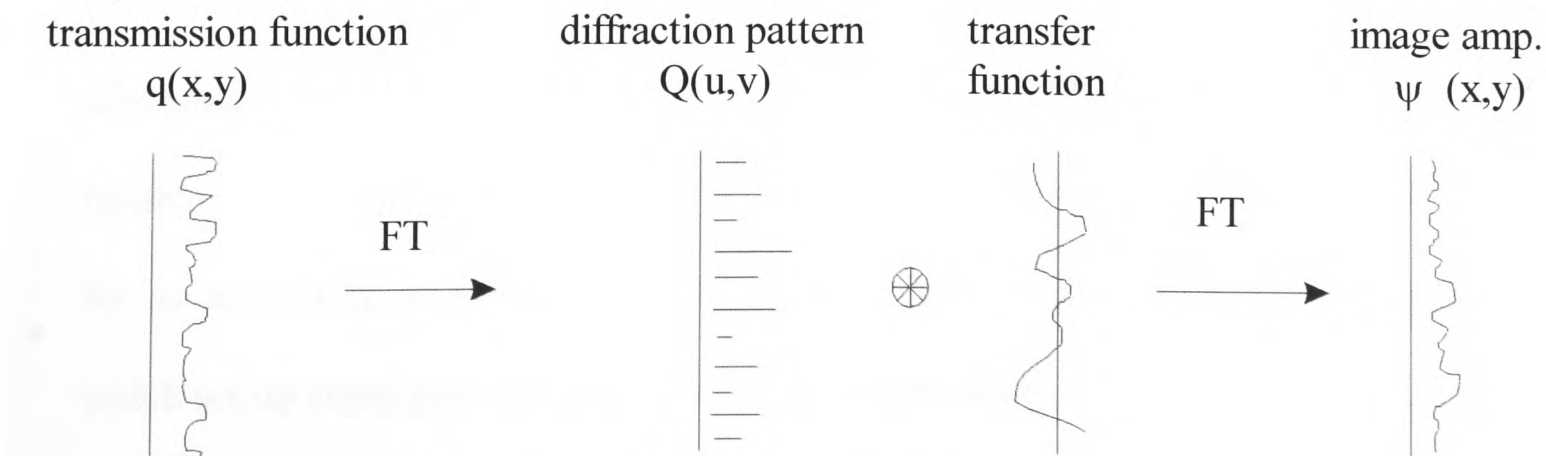


Figure 4.6 : Image formation as described by wave optics

The transfer function accounts for the fact that the image is not an exact reproduction of the transmission function of the specimen, but is affected by lens aberrations (distorting the relative phases) and finite apertures (cutting off waves at high scattering angles)

According to Abbé's theory, the theoretical resolution limit for an optical microscope is;

$$d = \frac{1.22\lambda}{\alpha} \quad (4.14)$$

However this is not the case for electron microscopy as the electrons are coherent and this relationship is only true for two incoherent sources. It is also impossible to make lenses free from aberrations (spherical and chromatic) or astigmatism. Spherical aberration is due to a lens being stronger at its edge, than close to its axis. Thus widely scattered rays are brought to a focus more quickly than those close to the axis. This results in a point in the object being imaged as a disk. Chromatic aberration is due to the variations in energy of the electron waves reaching the image plane (this results from fluctuations in accelerating voltage, electrons losing energy due to inelastic scattering, variations in objective lens current altering the focal length). Thus electrons of lower energy (longer λ) are focussed before electrons which have not lost energy. Astigmatism arises because a lens field is not perfectly symmetrical but is slightly elliptical as a result of inhomogeneities in the polepiece material or geometry. This effect is also exacerbated by local charging, dirty apertures or non-conducting specimens which can produce local electrostatic fields or magnetic specimens. The overall effect is that the lens field has different strengths around its axis, resulting in an object being imaged as a disc, or at worst a line. This must be compensated for as accurately as possible when imaging at high resolution work, using stigmator coils which set up equal and opposite fields to the elliptical fields producing the astigmatism.

4.2.1.1 Weak Phase Object Approximation

Compared with x-rays or neutrons of comparable wavelengths, electrons interact strongly with matter. For high resolution imaging it is the elastic scattering that is the most important, and so to avoid complications in image contrast it is necessary to use specimens of a thickness of the same order as the mean free path for elastic scattering.

Electron scattering angles are small, and thus as a first approximation we can assume that the change in phase of the electron depends on the distribution of potential along a straight line through the object. If such a potential is given by $\phi(xyz)$ then a plane wave passing through the specimen in the z-direction will undergo a phase change that is a function of the x-y co-ordinates, and proportional to the projection of the potential in the z-direction

$$\phi(xy) = \int \phi(xyz) dz. \quad (4.15)$$

The phase change (relative to transmission through vacuum $\phi=0$) is given by the product of ϕ and σ , where σ defines the strength of the interaction with matter and is equal to

$$\sigma = \frac{2\pi me\lambda}{h^2}. \quad (4.16)$$

The effect on the plane wave exiting the crystal is seen by multiplying the incident wave amplitude by the crystal transmission function

$$\Psi_E(xy) = \Psi_o(xy)q(xy) \quad (4.17)$$

where $\Psi_E(x,y)$ is the exit wave, $\Psi_o(x,y)$ is the incident wave and q is the crystal transmission function and is equal to

$$q = e^{-i\sigma\phi}. \quad (4.18)$$

Equation 4.17 is the *Phase Object Approximation* (POA). It assumes that the crystal is very thin, such that inelastic scattering events are negligible, and each electron is scattered only once during its traversal of the crystal. Inelastic scattering can scatter electrons outside the

aperture and hence produce an effect that appears as absorption. In the absence of inelastic scattering the crystal acts only as a phase object (POA) and affects only the phase not the amplitude of the beam. For a very thin object we can assume that changes in ϕ are small.

This is the *Weak Phase Object Approximation* (WPOA) and we can approximate q by

$$q = 1 - i\sigma\phi(xy). \quad (4.19)$$

The $i\sigma\phi(xy)$ term is the scattering function which gives rise to the distribution of scattered amplitude in the back focal plane. This shows that the scattered beam is always $\pi/2$ out of phase with the primary beam.

4.2.2.2 Imaging of a Weak Phase Object

As equation 4.17 states, the plane wave exiting the crystal can be described:

$$\Psi_E(x, y) = \Psi_O(x, y)q(x, y) \quad (4.20)$$

The intensity at the exit face is given by

$$I = |\Psi_E|^2 = 1. \quad (4.21)$$

and so for a perfect microscope there is no contrast in the image. However, electron microscopes are not perfect for the reasons already considered. The wave exiting from the specimen is convoluted with the transfer function of the microscope, which is a function of the defocus of the objective lens and the spherical aberration. The former effect leads to a relative phase change between different diffracted beams and the second introduces a phase factor dependent on spatial frequency. These lead to a multiplication of the electron wave by

$$T(u) = \exp(i\chi(u)) \quad (4.22)$$

where χ is the phase shift of the beam. Scherzer [5] derived the following expression between phase shift χ , diffraction angle θ , and defocus Δf :

$$\chi = \frac{\pi}{2\lambda}(C_s\theta^4 - 2\Delta f\theta^2) . \quad (4.23)$$

There are also two exponential damping terms resulting from defocus spread, chromatic aberration, C_c , spherical aberration, C_s , and beam divergence, α , which leads to a contrast transfer function, $T(u)$,

$$T(u) = \exp(i\chi) \exp^{-A} \exp^{-B} \quad (4.24)$$

$$A = f(\Delta f, C_c)$$

$$B = f(C_s, \alpha)$$

This function varies as $\sin \chi$, since $\cos \chi$ is 90° out of phase with the incident beam and therefore cannot produce interference effects. The result of χ is that different spatial frequencies within a specimen will be imaged with different contrast (i.e. for $\sin \chi = +1$ contrast is high and positive therefore scattering centres (atoms) would appear bright in the image. For $\sin \chi = -1$ contrast is high but negative and therefore atoms appear dark.

The optimum defocus is the value at which $\sin \chi$ is as close to -1 as possible, as this results in the largest possible range of spatial frequencies over which no change in contrast is introduced. This defocus is given by the Scherzer focus, Δf , where

$$\Delta f = -1.2\sqrt{C_s\lambda} . \quad (4.25)$$

The Scherzer resolution is

$$d_o = 0.66C_s^{1/4}\lambda^{3/4} . \quad (4.26)$$

These values are fixed for a given microscope and are independent of the specimen. The phase shift χ , at Scherzer defocus, is shown plotted against inverse spacing in Figure 4.7 (with the damping terms ignored).

In summary, if a sufficiently thin crystalline specimen is appropriately oriented so that the electron beam is exactly parallel to low index lattice planes (this is achieved by

tilting the specimen whilst observing the selected area diffraction, SAD, pattern) then at Scherzer defocus dark rows of dots may be obtained which are directly interpretable in terms of projected atomic structure.

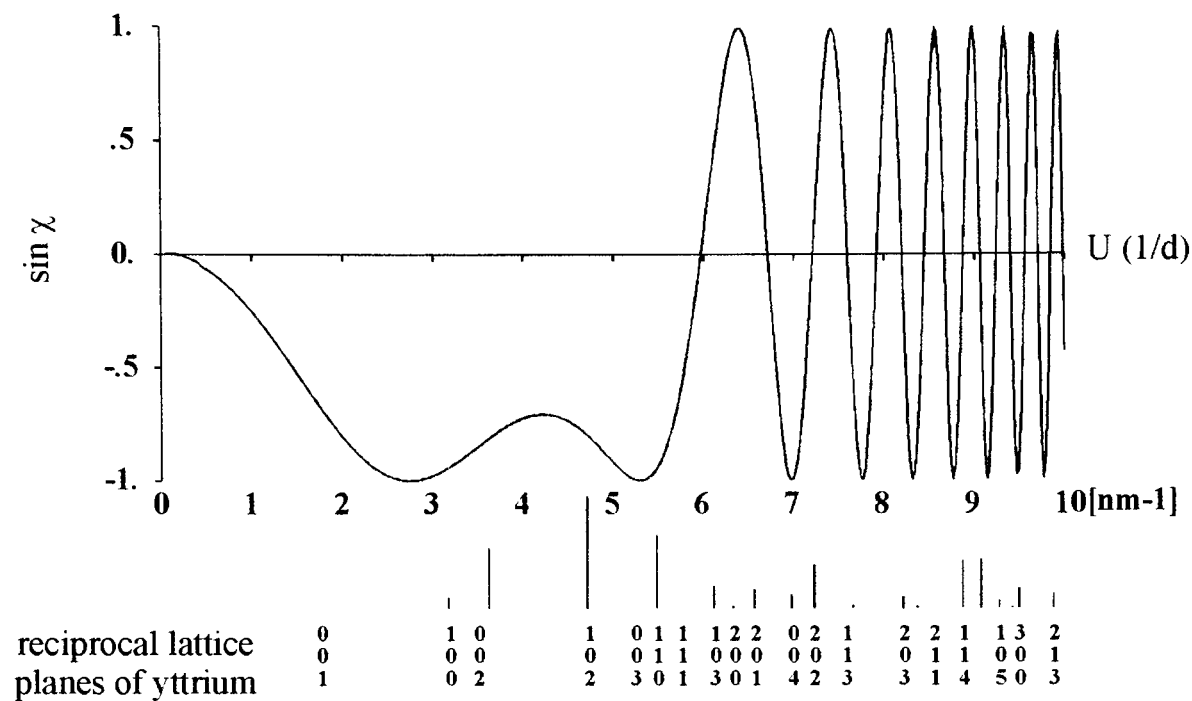


Figure 4.7 : Contrast transfer function for a JEOL 4000EX microscope, operating at 400kV, with the reciprocal lattice planes of yttrium shown

4.2.2.3 Failure of the Weak Phase Object Approximation

However this simple discussion of the WPOA fails badly in many cases where dynamical scattering effects are strong and the kinematic approach is too simplistic. Dynamical scattering events means that a beam may be diffracted more than once when passing through a crystal. Thus multiple scattering events continually vary the phase and magnitude of the beam, as other beams are scattered into the beam, and the beam itself suffers scattering events which reduce its initial intensity. This means that dynamical scattering is very different from the single scattering case, and although the angles of scattering are fixed thus defining the same periodicities within the crystal, the intensities are now modified by the phase changes incurred by the multiple scattering events.

The validity of the kinematical approximation depends strongly on the crystal orientation and on the scattering potential. The POA neglects the spreading of the wave by

Fresnel diffraction, which is on the scale $(R\lambda)^{1/2}$. If this spread is comparable to the interatomic distances then the POA is poor. For light atom crystals, the approximation is valid for very small thicknesses, however for medium-heavy weight crystals there is evidence that channelling effects occur when the incident beam is parallel to a zone axis. This confines the electron paths to atom rows and thus the POA may be valid for greater thickness' (10nm for 100keV electrons).

The WPOA assumes both kinematic and POA approximations. It fails for 0.5-1nm thickness for heavy Z materials because the kinematic approximation is no longer valid, and for light Z materials due to the spreading of the wave by Fresnel diffraction.

4.2.2.4 Image simulations

Real specimens are almost never good approximations of a WPO. Thus the dynamical interactions between diffracted and incident beams must also be considered. This results in the contrast being highly dependent on specimen thickness and defocus and it is therefore usually impossible to draw direct conclusions about the crystal structure directly from the electron micrographs. Computer simulations of the assumed model of crystal structure for a series of defoci and a number of thicknesses enable comparison between simulated and experimental images to be made. If there are discrepancies between the two then the model can be modified. In this way it is possible to determine the atomic model, for example at interfaces. The software package used for this work was EMS [6]. There are several methods to calculate the images, and the texts referenced in this section discuss the various methods more fully. All methods are however basically equivalent, and should give the same results when correctly applied. EMS software uses the multislice method (explained below) as this is the most convenient form for computer calculations.

4.2.2.5 The Multislice approach

This approach calculates the scattering from ideal 2-dimensional objects. Such an approach is often much more appropriate for HREM than methods such as the Bloch wave method that assumes infinite periodic crystals. The approach accounts for the phase change due to the potential and the Fresnel dispersion of the wave by separating the two effects. The crystal is divided into a series of slices, assuming that the phase change acts at a series of planes Δz apart, and the diffraction is assumed to act within these planes. As $\Delta z \rightarrow 0$ the application of these two effects is combined into one simultaneous operation.

The multislice method is useful for computer calculations of the diffracted amplitudes. Firstly the crystal is divided into a finite number of slices, then the diffraction amplitudes are obtained by modulating the phase by the POA and multiplying the amplitude by the Fresnel diffraction phase factor. This process is iterated a number of times. If slice thicknesses are 0.3-0.4 nm then the POA is valid and thus this is a reasonable method for calculating intensity.

4.2.2 RHEED

Reflection high energy electron diffraction, RHEED, is an important characterisation tool used in-situ during MBE growth to give real time information about the quality of surface preparation, the orientation of the crystal, and the crystal structure and morphology of the growth surface throughout deposition. A simple explanation of the

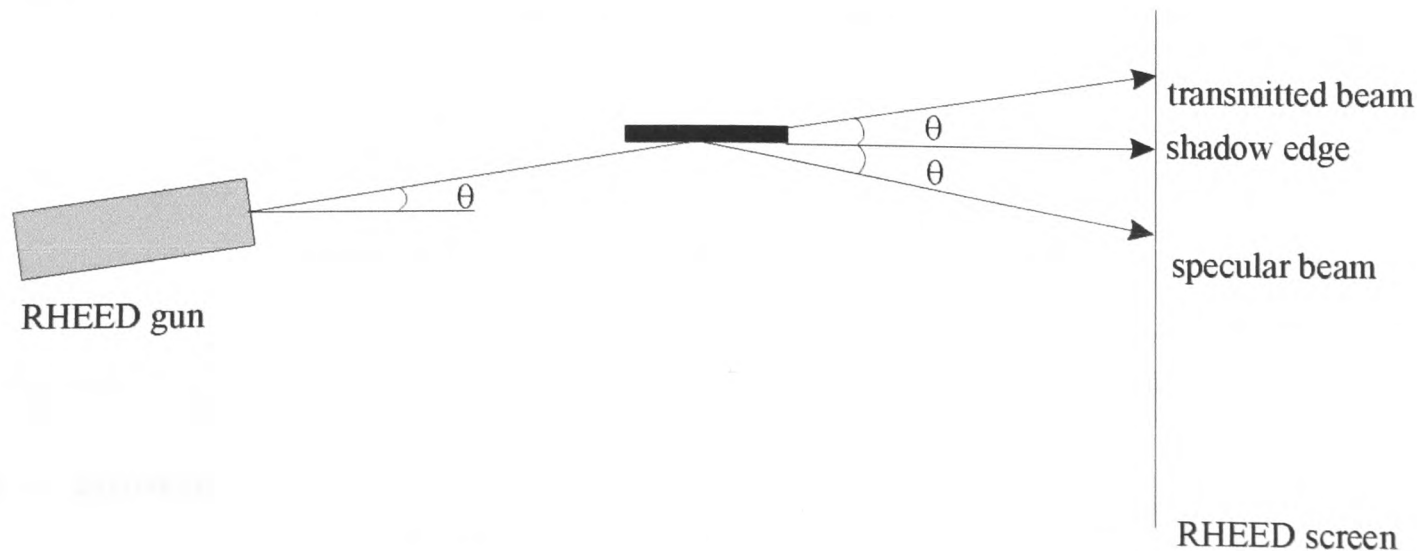


Figure 4. 8 : The geometry of the RHEED apparatus

formation of RHEED images is given here, with reference given to other texts for a more exhaustive discussion [7-9]. Electrons are accelerated to 20 keV and are incident on the substrate at a variable glancing angle, normally about 1° . Diffraction of the incident beam leads to streaks normal to the shadow edge of the sample superposed on a fairly uniform background which is a result of inelastically scattered electrons. As Figure 4.8 shows, the geometry of the RHEED apparatus make it ideal for inclusion within the MBE chamber.

The low angle of incidence restricts the penetration of the electrons to the outermost atomic layers, and so the interaction of the electron beam is essentially with a 2-dimensional atomic net. In the case where the third dimension in real space is missing, the third dimension in reciprocal space is also not defined (equations 4.3). Therefore the reciprocal lattice construction of the surface consists of rods perpendicular to the real surface. The radius of the Ewald sphere is much greater than the separation of the rods, as shown by the following calculation, where;

$$\text{Radius of sphere} = \frac{2\pi}{\lambda} = \frac{\sqrt{2mE}}{\hbar} = 7.22 \times 10^{11} \text{ m}^{-1}, \text{ where } \lambda \text{ (20keV electrons)} = 8.7 \times 10^{-12} \text{ m}$$

$$\text{Separation of rods} = \frac{2\pi}{a_0} = 1.9 \times 10^{10} \text{ m}^{-1}$$

where a_0 is the lattice parameter. Thus the rods intersect the Ewald sphere on an almost flat surface as shown in Figure 4.9.

The type of pattern obtained is indicative of the nature of the growing surface. A monochromatic electron beam interacting with an atomically smooth growing surface will yield a diffraction pattern of spots located on Laue circles. However when atomic steps limit the number of atomic rows that will scatter coherently, or the beam is not perfectly monochromatic, then the RHEED pattern will show streaks, as both the reciprocal lattice rods and the Ewald sphere have a finite thickness and intersect along their length. If the surface is growing in islands, then the electrons will be diffracted in transmission through

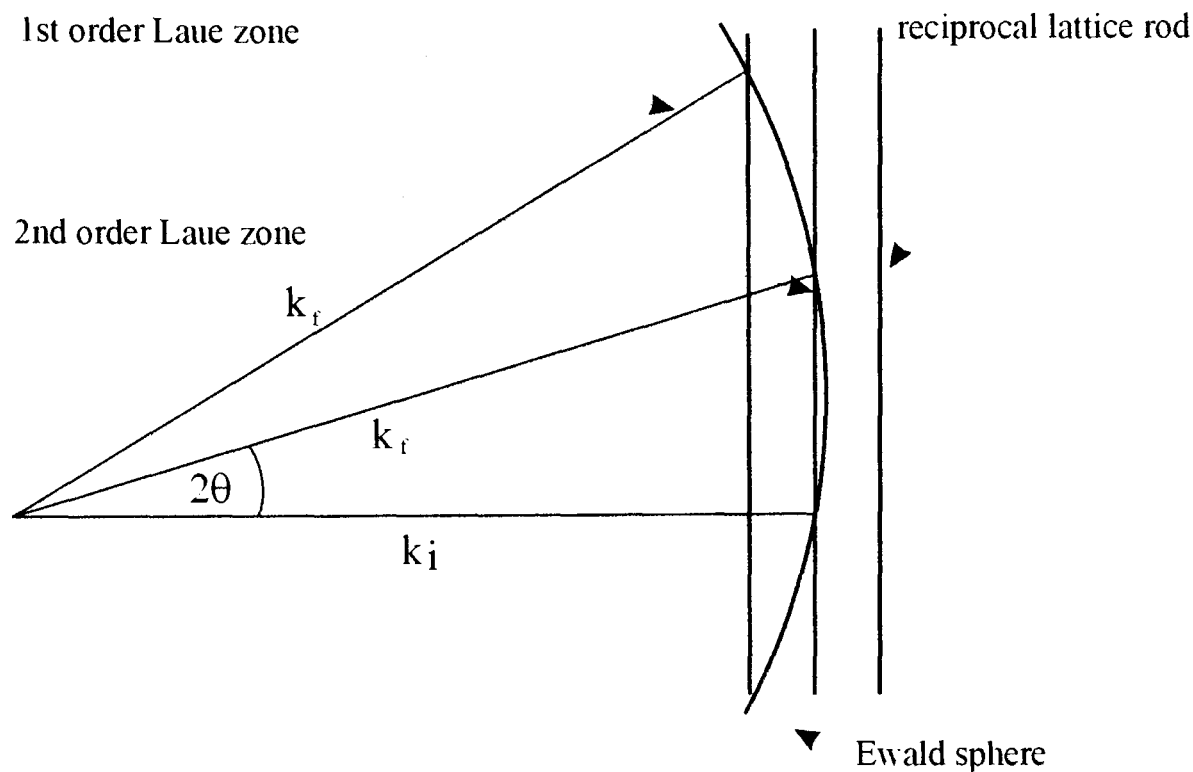


Figure 4.9: Ewald sphere construction explaining qualitatively the formation of streaks in the RHEED pattern.

the islands and the resulting pattern is a 3-dimensional spot pattern. A schematic diagram illustrating how RHEED patterns formed by different surfaces is shown in Figure 4.10, with real examples of RHEED images shown in Figure 4.11. The RHEED pattern of the $(1\bar{1}20)_{\text{Al}_2\text{O}_3}$ surface along the $[0001]_{\text{Al}_2\text{O}_3}$ azimuth is shown in Figure 4.11(a). Typical of a high quality surface, the pattern exhibits several Kikuchi lines, which arise from the subsequent elastic scattering in the bulk crystal of electrons which had previously been inelastically scattered at the surface. The presence of Kikuchi lines is indicative of good bulk crystallinity in the near surface region. A typical RHEED pattern of a growing surface is shown in Figure 4.11(b), the streaked pattern shows that the terminating layer is not atomically smooth, but in fact has a limited number of atomic steps on the surface. The spacing of the streaks is inversely proportional to the spacing of the atomic rows parallel to the direction of the beam. Thus by using the sapphire substrate as a reference calibration it is possible to measure with this technique the d-spacing of in-plane atomic rows along different azimuthal directions.

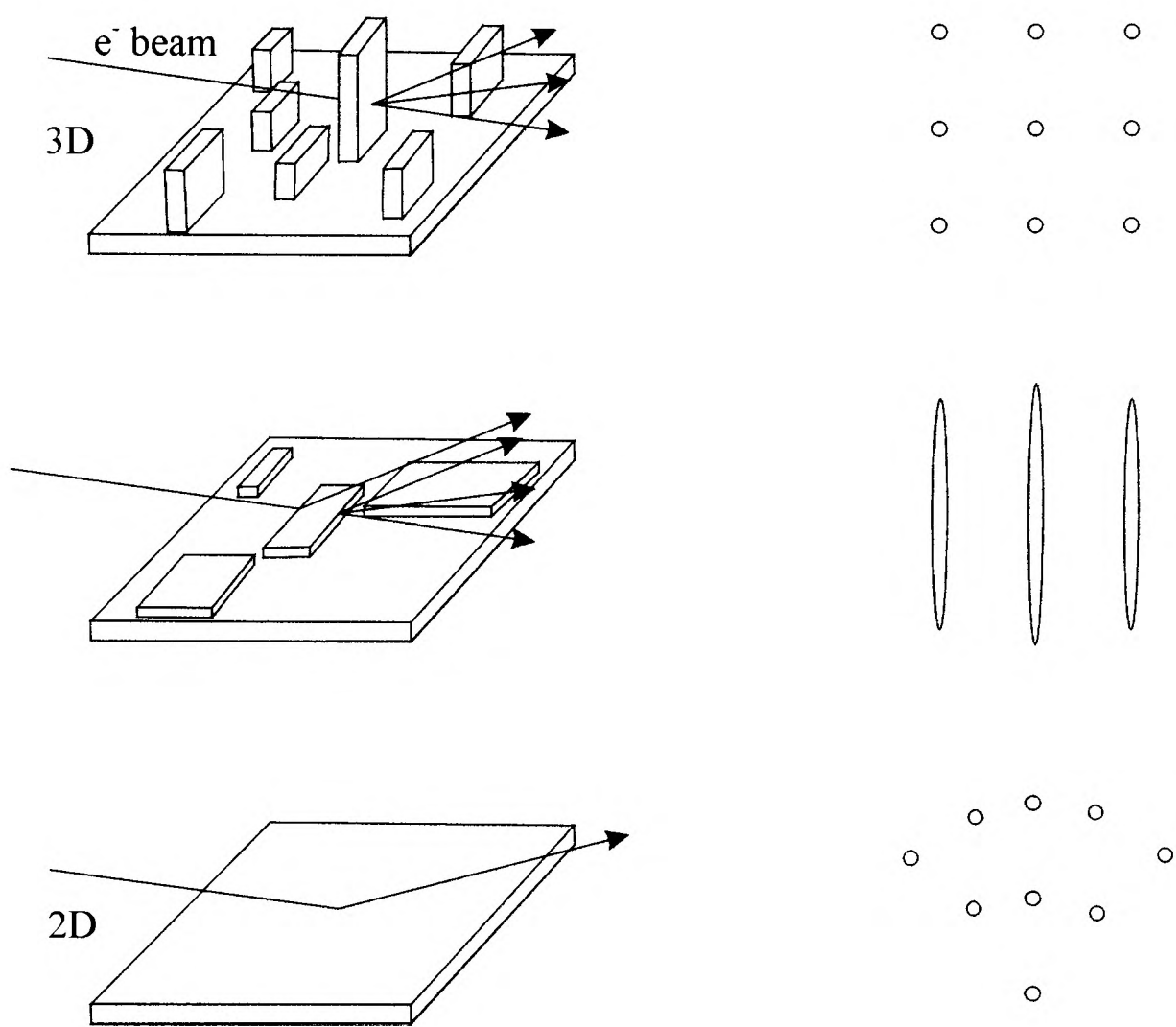


Figure 4.10 : Examples of how different surfaces affect the RHEED diffraction pattern

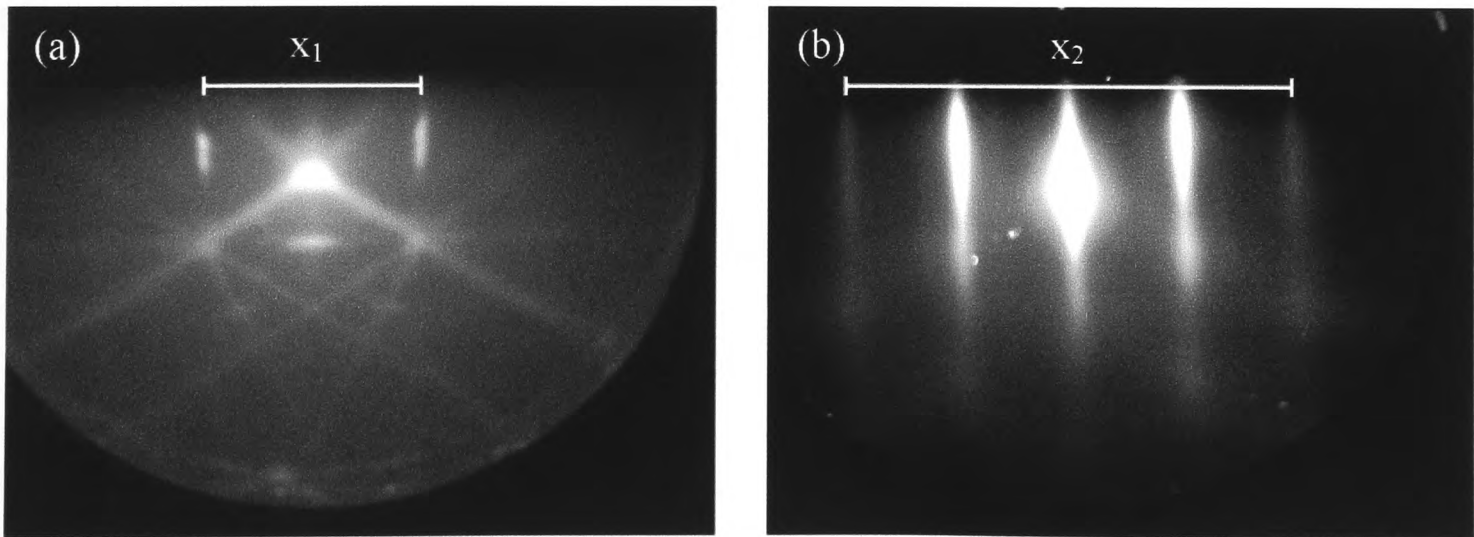


Figure 4.11: (a) RHEED pattern taken along the $[0001]$ direction in sapphire, x_1 is inversely proportional to the spacing of the atoms along $[\bar{1}100]$ i.e. $\sqrt{3} / a = 3.64 \times 10^{-9} \text{ m}^{-1}$ (b) RHEED pattern taken along the $[1\bar{1}1]$ direction in Nb, x_2 is inversely proportional to the spacing of the atoms along $[\bar{1}12]$ i.e. $\sqrt{6} / a = 7.42 \times 10^{-9} \text{ m}^{-1}$

As already mentioned RHEED can also be used to give real time information about the growth morphology of the surface. This is achieved by monitoring the intensity in the specular beam. Such a method is capable of detecting in-situ the growth rate in the case of Frank-van der Merwe (2D) growth. This is because the reflectivity, and therefore the intensity in the specular beam, is at a maximum when the surface is atomically smooth, and a minimum when the surface is maximally disordered. Thus if the system is growing monolayer-by-monolayer then the intensity in the specular beam is seen to oscillate, with one oscillation corresponding to the deposition of a complete monolayer. It is not possible to use RHEED to give real time information on the growth rate for SK or VW growth modes as the oscillations in the specular beam are no longer visible.

4.3 HREM specimen preparation

This section describes the techniques used to produce samples suitable for electron microscopy. The ideal specimen is electron transparent (i.e. the thickness is of the same order as the mean free path for elastic scattering, typically 10s of nanometers) and representative of the bulk sample.

4.3.1 Conventional Specimen Preparation

The method used is adapted from the method published by Newcomb [10]. It is a general method that can be used when the interface of interest has to be cut from a bulk sample. The specimens are prepared in cross-section so that the relevant interfaces lie vertically in the foil. Essentially the specimen is mounted in a slotted rod, which is itself enclosed in a supporting outer tube of diameter 3mm. Firstly the sample (dimensions 10mm x 12mm x 1mm) is cut with a diamond saw into 4mm x 2mm x 1mm rectangles. The pieces are then glued together with the layers facing, using M-Bond epoxy (Figure 4.12(a)). This

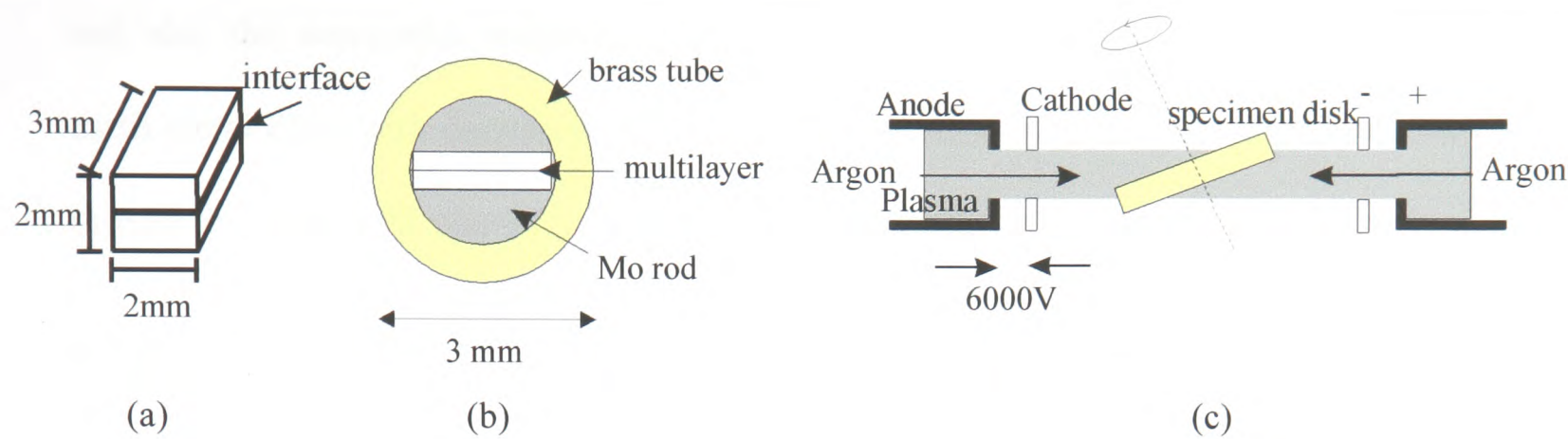


Figure 4.12 : Conventional TEM specimen preparation

protects the metal layer during later stages of preparation. The sapphire on either side of the interface is then ground on a 12 μm diamond wheel until the sandwich is 250 μm thick. Then the sandwiches are glued with Araldite into a slit within a 2mm diameter molybdenum rod which is supported by a thin brass tube of outer diameter 3mm (Figure 4.12(b)). 500 μm thick discs are cut from these samples and mounted with a low melting point ($\sim 50^\circ\text{C}$) wax on a steel cylinder. They are ground on a rotating 12 μm diamond wheel to a thickness of 80 μm . One side is polished with a 6 μm polishing lap, as a relatively scratch free surface is important for ion beam thinning since a rough surface encourages differential etching. The sample is then dimpled to a thickness of around 30 μm . The final stage of preparation is ion beam milling. The sample is cooled to liquid nitrogen temperature under vacuum. This minimizes atom migration on the specimen and also contributes to cryopumping the vacuum. Ar gas is bled into a chamber where a potential between 4-6keV creates a beam of Ar ions that impinge on the rotating specimen, inclined at a shallow angle to reduce damage to the specimen, (Figure 4.12(c)).

4.3.2 Focussed Ion Beam Specimen Preparation

A focussed ion beam, FIB, system was also used to prepare samples, as recent advances in the methods of preparing TEM samples with a FIB system [11,12] have enabled site-specific cross-sectional preparation, the preparation of plan view specimens

and also the successful preparation of rare earth metal samples. The preparation of rare earth metal films with conventional techniques proved impossible due to the reaction of the rare earth metals with water (or hydrogen) to form rare earth hydrides.

4.3.2.1 The system

The FIB system operated much like a scanning electron microscope. A gallium reservoir is in contact with a sharp tungsten needle. The Ga wets the W needle and flows to the tip. A high extraction field is applied to pull the liquid into a sharp cone (radius 5-10nm). Ions are emitted from the tip and accelerated down the FIB column. The ions are used for milling, and secondary ions are detected for imaging. The system operates between 5-30keV and by varying the lens strength and aperture size, the probe current (and hence the beam diameter) can be altered from tens of picoamps to several nanoamps (corresponding to beam diameters of 5nm - 0.5 μ m).

4.3.2.2 Cross-sectional samples prepared by the "lift-out" technique

This technique involves no pre-FIB preparation as the bulk specimen is inserted into the FIB system. The first stage is to locate a suitable region and then to deposit a platinum strap ($\sim 1.5\mu$ m thick) to protect the area of interest from erosion during the milling process. The second stage is to mill staircase shaped trenches ($10 \times 10\mu$ m, final depth 8μ m) from either side, leaving a membrane $\sim 0.5\mu$ m thick. This stage employs fairly high beam currents of 3000-5000pA. The initial clean-up of the samples is done with smaller beam currents (300-500pA), with the sample being tilted to $\pm 1.5^\circ$ for front/back thinning to minimise the taper in cross-section that arises because of the beam profile. Prior to final thinning the sample is tilted to 45° and the base and one side are cut free. The sample is tilted back to the starting position and thinned to electron transparency. The last step before cutting the remaining side is a low energy clean ($I = 80$ pA, $V = 5$ kV) to reduce the damage caused by milling. The

sample is "plucked" from the bulk material using the static charge on a fine glass needle. The membrane is then placed on a Formvar, holey carbon or copper grid. This preparation process is shown in Figure 4.13.

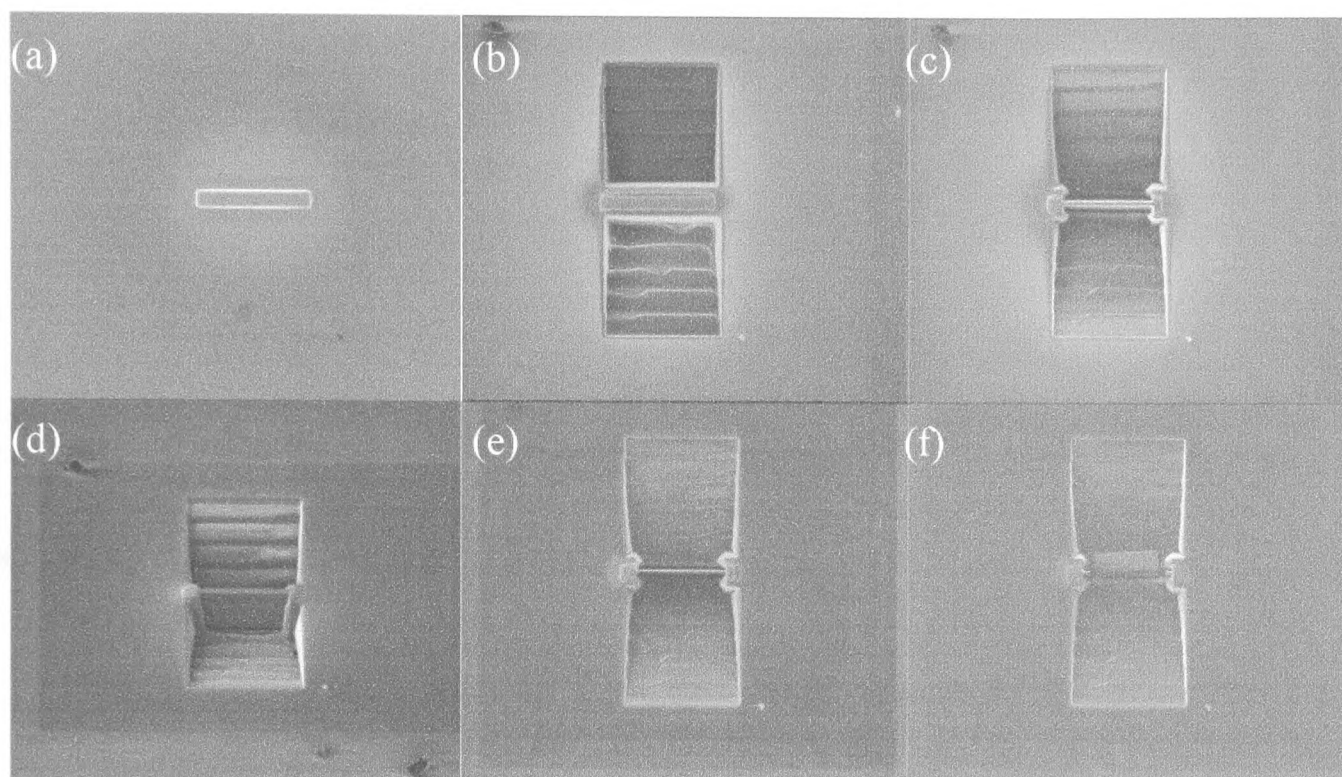


Figure 4.13 : the FIB preparation of a TEM membrane (a) deposition of Pt strap (b) milling of staircases (c) initial clean-up performed at $\pm 1.5^\circ$ (d) the base and one side are cut at a sample tilt of 45° (e) final low energy clean (f) cut remaining side to leave free membrane

4.3.2.3 Plan view samples, by the "pre-thinning" technique

Plan view specimens require an electron transparent window in the substrate, whilst leaving the film itself intact. Therefore it is necessary to first extract a sample small enough to fit in the TEM. This is achieved by cutting the bulk specimen into 2x2 mm squares, and then back-thinning the sapphire on a 12 μm diamond wheel, until it is of order 100 μm thick. The squares are then cleaved, to ensure a clean edge for milling, and mounted on a copper slot grid. The specimen preparation in the FIB is then identical with the cross-sectional

samples, but with milling only occurring from one side. A schematic diagram of the specimen after thinning is shown in Figure 4.14.

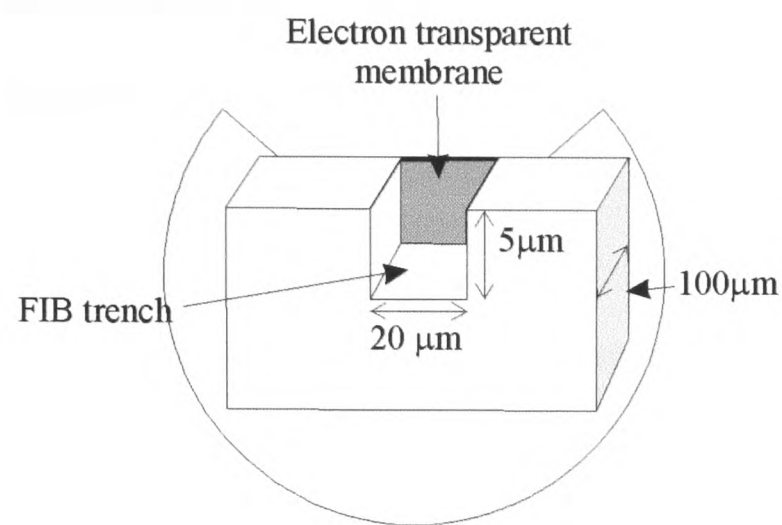


Figure 4.14 : schematic diagram of plan view FIB TEM sample

4.4 Scanning Probe Techniques

The following two sections discusses some aspects of scanning probe microscopy. For a more detailed overview of the subject reference is made to the book on scanning probe microscopy by Wiesendanger [13].

4.4.1 Atomic Force Microscopy

An atomic force microscope is essentially a hybrid between a surface force apparatus, SFA, which is capable of measuring surface forces to high precision but gives no spatial resolution, and a surface profilometer, which allows detailed mapping of the surface topography. A schematic drawing of an atomic force microscope is shown in Figure 4.15.

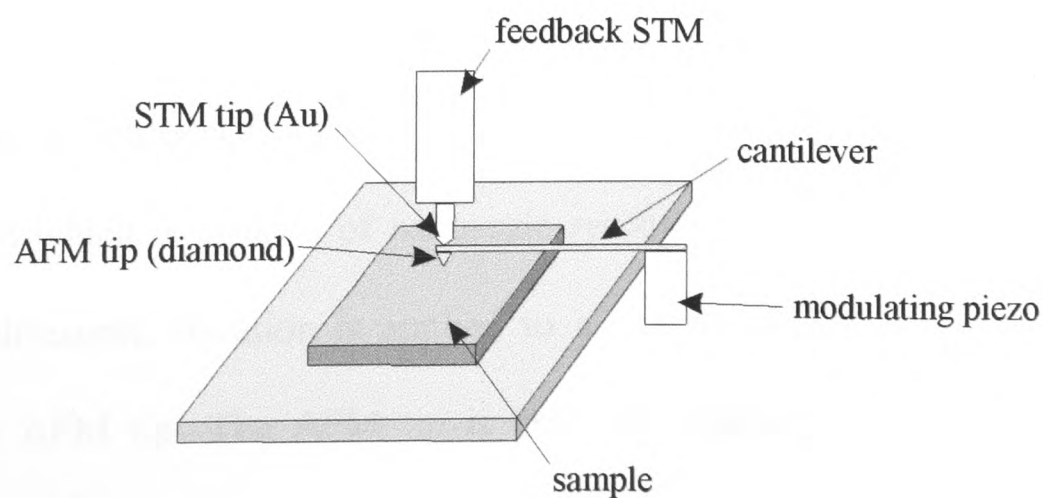


Figure 4.15: Schematic diagram of Atomic force microscope

Essentially a probe tip is mounted on a cantilever type spring, and this is then lowered towards the sample. For two electrically neutral and non-magnetic bodies separated by a distance of tens of nanometers the interaction force between them is dominated by the van der Waals forces, and this force to a first approximation can be assumed to be

$$\mathbf{F}_{VDW}(s) \propto -\frac{1}{s^6} \quad (4.27)$$

where s is the separation of the bodies. The force between the sample and the tip causes the lever to deflect (Δz) according to Hooke's Law,

$$\mathbf{F} = c \cdot \Delta z \quad (4.28)$$

where c is the spring constant. These deflections are measured by a scanning tunnelling microscope tip located within tunnelling distance of the cantilever. (In STM a bias voltage is applied between a sharp metal tip and a conducting sample, and when the two are separated by a small distance, $\sim 0.1\text{nm}$, a tunnelling current flows due to quantum mechanical tunnelling before mechanical contact is made between the two materials. By keeping the tunnelling current constant by means of a feedback loop, which to a first approximation remain constant at constant distance from the tip, it is possible to follow the contours of a surface, or in this case the deflections of the cantilever). A topographic image of the sample is obtained by keeping the force on the AFM tip constant.

4.4.2 Ultrasonic Force Microscopy

An ultrasonic force microscope, UFM, [14,15] is a combination of an acoustic microscope, which is sensitive to the elastic properties of the material, and an atomic force microscope which is capable of nanoscale resolution imaging. In a UFM a high frequency ($\sim \text{MHz}$) ultrasonic vibration is applied to a sample, which is then forced to indent itself against an AFM tip. The AFM tip is held in a static position, and the contact between

sample and tip acts as a mechanical diode, which is able to detect the amplitude-modulated ultrasonic vibrations in the kHz frequency due to the extreme stiffness of the cantilever at the indentation frequency. The principle of detection is shown in Figure 4.16.

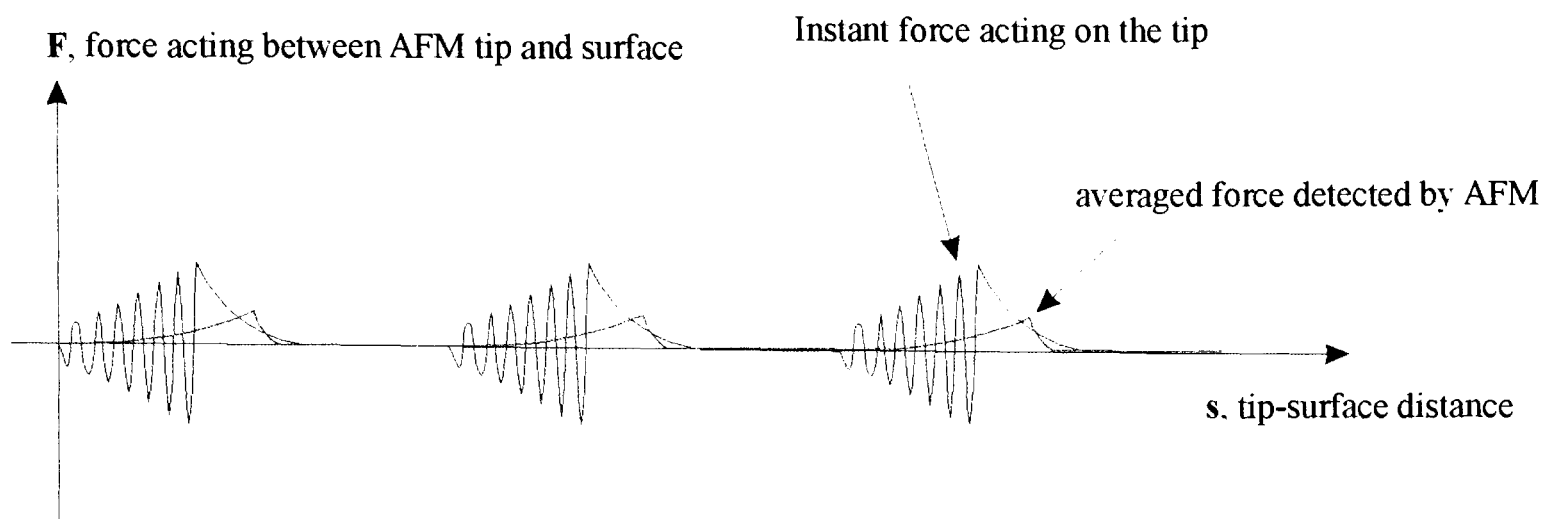


Figure 4.16: Principle of non-linear detection of ultrasonic vibration in UFM

4.5 Neutron Diffraction

In a neutron scattering experiment the chemical and magnetic structure of a crystal can be deduced by measuring the probability with which neutrons with a wave vector $\mathbf{k}_i$ are scattered into the state with wave vector $\mathbf{k}_f$, as shown in Figure 4.17. Thus the intensity of the scattered neutrons is measured as a function of the momentum transfer, $\mathbf{Q}$

$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f . \quad (4.29)$$

As the energy of the neutrons is

$$E = \hbar\omega = \frac{\hbar^2}{2m_n} \mathbf{k}^2 \quad (4.30)$$

the corresponding energy transfer is given by;

$$\hbar\omega = \frac{\hbar^2}{2m_n} (\mathbf{k}_i^2 - \mathbf{k}_f^2) \quad (4.31)$$

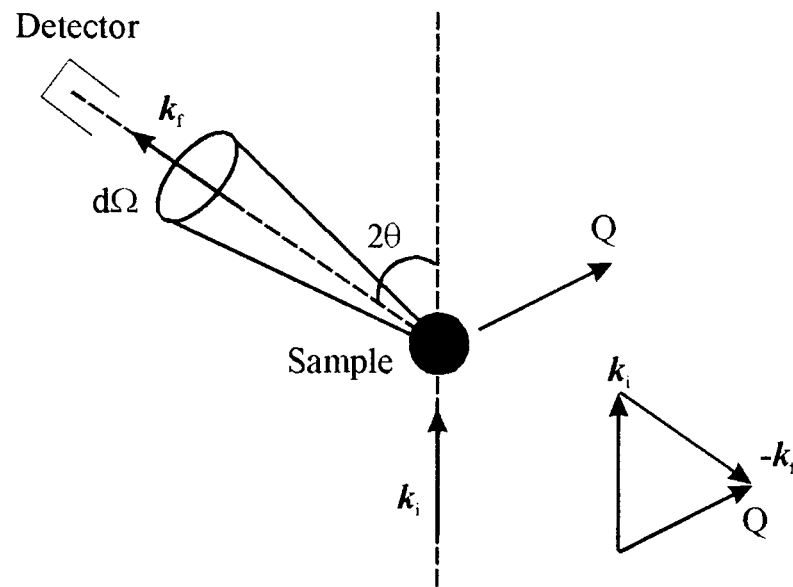


Figure 4.18: The geometry of a typical scattering process

Interactions occur between the neutron and the nucleus, and also between the magnetic dipole moment associated with the neutron and with electrons in unfilled shells. These interactions give rise to scattering referred to as nuclear and magnetic respectively.

4.5.1 Neutron-nuclear scattering

The neutron-nucleus interaction occurs via the strong nuclear force, which may be described by the Fermi pseudo-potential, which for a rigid array of atoms at positions $\mathbf{R}_l$ is given by

$$V(\mathbf{r}) = \left(\frac{2\pi\hbar^2}{m} \right) \sum_l b_l \delta(\mathbf{r} - \mathbf{R}_l). \quad (4.32)$$

b_l is the scattering length and is a measure of the scattering strength of a particular nuclide. To determine the scattering cross-section an average over all final states is taken, keeping the initial state fixed, then an average over all possible initial states is taken. This is then integrated over all final energies to find $(d\sigma/d\Omega)$. This is the sum of a coherent and incoherent term

$$\left(\frac{d\sigma}{d\Omega} \right) = \left(\frac{d\sigma}{d\Omega} \right)_{inc} + \left(\frac{d\sigma}{d\Omega} \right)_{coh} \quad (4.33)$$

where

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh} = \left| \sum_i b_i e^{i\mathbf{Q}\cdot\mathbf{r}_i} \right|^2. \quad (4.34)$$

This scattering involves interference effects from the scattering of different nuclei and is thus referred to as the coherent scattering term. By summing over all $\mathbf{R}_l$ atomic positions in a crystal

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh} = \frac{(2\pi)^3 N}{V} \sum_{\mathbf{Q}} |F_N(\mathbf{Q})|^2 \delta(\mathbf{Q} - \mathbf{g}) \quad (4.35)$$

where the crystal consists of N unit cells of volume V , $\mathbf{g}$ is a reciprocal lattice vector, F_N the nuclear structure factor which for l atoms in the unit cell

$$F_N(\mathbf{Q}) = \sum_l b_{coh} e^{i\mathbf{g}\cdot\mathbf{R}_l}. \quad (4.36)$$

From the delta function $(d\sigma/d\Omega)$ is zero unless $\mathbf{Q}=\mathbf{g}$. Given this, and the scattering triangle in Figure 4.17, it is possible to derive the Bragg condition for coherent elastic scattering (equation 4.1).

For a real non-rigid lattice, the mean displacement of an atom from its equilibrium position must be accounted for. This is achieved by the Debye-Waller factor, $e^{-2W(\mathbf{Q})}$, where $2W(\mathbf{Q})$ is the mean square displacement of the nucleus from its equilibrium position multiplied by $\mathbf{Q}$. This has the effect of redistributing the scattered intensity away from the Bragg positions and is significant when comparing peaks over wide temperature ranges.

The incoherent cross-section is isotropic, independent of $\mathbf{Q}$ and depends primarily on the spin state of a nuclei. In the neutron scattering experiments presented in chapter 9 on the magnetic structure of HoD_{2+x} the incoherent scattering is a source of background scattering to the measurement of the coherent-elastic scattering. Deuterium was used in preference to hydrogen because it has a much smaller incoherent cross-section than hydrogen.

4.5.2 Magnetic neutron scattering

An appropriate form of the interaction potential is found by considering the magnetic moment of the neutron, which is

$$\boldsymbol{\mu}_N = -\gamma\mu_N \boldsymbol{\sigma} \quad (4.37)$$

where γ is the gyromagnetic factor, μ_N the nuclear magneton and $\boldsymbol{\sigma}$ the neutron spin vector. This magnetic moment gives rise to a vector potential which interacts with the moments on the ions in the solid. The intensity of scattered neutrons measured as a function of $\mathbf{Q}$ is given by

$$I(\mathbf{Q}) = \sum_{\alpha,\beta} \langle (\delta_{\alpha\beta} - \hat{\mathbf{Q}}_\alpha \cdot \hat{\mathbf{Q}}_\beta) F^\alpha(\mathbf{Q}) F^\beta(\mathbf{Q}) \rangle \quad (4.38)$$

where α and β index the Cartesian axes x,y,z, $\delta_{\alpha\beta}$ is the Kronecker delta, the $\langle \rangle$ denotes the domain average and $\hat{\mathbf{Q}}_\alpha$ is the α th component of the scattering vector, and F

$$F_m = \sum_j \mu_j^\alpha f_j(\mathbf{Q}) e^{i\mathbf{Q} \cdot \mathbf{r}_j} \quad (4.39)$$

where j labels the magnetic moments in the unit cell, μ_j^α is the α th component of the j th moment, $f_j(\mathbf{Q})$ is the form factor for that moment, with values for the form factor given in the International Tables for Crystallography [16], and $\mathbf{r}_j$ is the position of that moment. $f_j(\mathbf{Q})$ shows that there is an important difference between the magnetic and nuclear scattering case, as the magnetic scattering is dependent on $\mathbf{Q}$ whereas for nuclear scattering it is not. This is because the neutron-nuclear scattering length b can be considered to be independent of $\mathbf{Q}$ due to the very small size of nuclear dimensions compared with the wavelengths of the neutrons, whereas the electrons responsible for the magnetic moment have a real spatial extent and hence the magnetic scattering function is not a delta function. The result $(\delta_{\alpha\beta} - \hat{\mathbf{Q}}_\alpha \cdot \hat{\mathbf{Q}}_\beta)$ contains the important result that the neutron is only sensitive to

the components of the moments that are perpendicular to the direction of the wave vector transfer.

For a collinear arrangement of spins, that is all $|\mu|$ are the same, this equation simplifies to

$$I(\mathbf{Q}) = \mu^2 (1 - (\hat{\mathbf{Q}} \cdot \hat{\mu})^2) \left| \sum_j \sigma_j f_j(\mathbf{Q}) e^{i\mathbf{Q} \cdot \mathbf{r}_j} \right|^2 \quad (4.40)$$

where $\sigma_j = \pm 1$.

References

- [1] J. M. Cowley "Section 4.3 Electron scattering", in *International tables for crystallography, Vol. C: Mathematical, Physical and Chemical Tables*, ed. 2., edited by A. J. C. Wilson, Kluwer academic publishers, Dordrecht, 223 (1995).
- [2] J. C. H. Spence *Experimental High-resolution Electron Microscopy*, 1 ed., Oxford University Press, Oxford, (1980).
- [3] *High-Resolution electron microscopy and associated techniques; Vol.*, edited by P. Buseck, J. M. Cowley, and L. Eyring Oxford University Press, New York, 1992.
- [4] P. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whelan *Electron microscopy of thin crystals*, 2 ed., Robert E. Krieger, New York, (1977).
- [5] O. Scherzer, *Appl. Phys.* **20**, 20 (1949).
- [6] P. A. Stadelman, *Ultramicroscopy* **21**, 131 (1987).
- [7] A. S. Arrott "Introduction to Reflection High Energy Electron Diffraction (RHEED)", in *Ultrathin Magnetic Structures I, Vol. 1*, edited by J. A. C. Bland and B. Heinrich, Springer-Verlag, (1994).
- [8] K. Yagi "RHEED and REM", in *Electron Diffraction Techniques, Vol. 2*, edited by J. M. Cowley, Oxford University Press, New York, 260 (1993).

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- [9] *Reflection High-Energy Electron Diffraction and Reflection Electron Imaging of Surfaces*; Vol. 188, edited by P. K. Larsen and P. J. Dobson Plenum Press, New York, 1988.
- [10] S. B. Newcomb, C. B. Boothroyd, and W. M. Stobbs, *J. Mic.* **140**, 195 (1985).
- [11] L. A. Giannuzzi and F. A. Stevie, *Micron* **30**, 197 (1999).
- [12] D. M. Schraub and R. S. Rai, *Prog. Crystal Growth and Charac.* **36**, 99 (1998).
- [13] R. Wiesendanger *Scanning probe microscopy and spectroscopy: methods and applications*, 1 ed., Cambridge University Press, Cambridge, (1994).
- [14] O. V. Kolosov, *Materials World* 753 (1998).
- [15] O. V. Kolosov, M. R. Castell, M. R. Marsh, G. A. D. Briggs, T. I. Kamins, and R. S. Williams, *Phys. Rev. Lett.* **81**, 1046 (1998).
- [16] P. J. Brown "Section 4.4.5 Magnetic form factors", in *International tables for crystallography, Vol. C: Mathematical, Physical and Chemical tables*, ed. 2., edited by A. J. C. Wilson, Kluwer academic publishers, Dordrecht (1995).

Chapter 5

The (110) Niobium || (11 $\bar{2}$ 0) Sapphire Interface

This chapter presents an investigation into the microstructural properties of the $(110)_{Nb} || (11\bar{2}0)_{Al_2O_3}$ interface using the combined techniques of reflection high energy electron diffraction, RHEED, high resolution electron microscopy, HREM, and conventional transmission electron microscopy. Section 5.1 describes the motivation behind the understanding of this system, and the basic crystallography of the system. Section 5.2 details the experimental techniques employed. Section 5.3 presents the results. Section 5.3.1 presents the results from in-situ RHEED experiments on the growing surface, and section 5.3.2 presents the results of electron microscope investigations of the interface, with section 5.3.1.1 discussing the coherent regions of the interface and section 5.3.2.2 discussing incoherent regions of the interface. Section 5.4 is a brief conclusion.

5.1 Introduction

The (110) Nb on (11 $\bar{2}$ 0) sapphire substrate system enabled the growth of the first high quality single-crystal metal superlattice of Nb/Ta [1] and has since been successfully employed as a substrate in MBE growth of rare earth [2-4] and transition metal superlattices [5] and most recently, for epitaxial films of Laves phase intermetallic compounds [6]. However for successful studies of the magnetic properties of such superlattice systems

smooth epilayers with atomically flat interfaces are required, and inevitably the quality of the niobium layer will influence how well the rest of the structure will grow. At the sapphire-niobium interface the lattice parameters and structures of the two materials differ and a stress develops within the material which must be relieved. Usually this strain relief is achieved either by the introduction of defects, such as dislocations, or by roughening of the surface. Understanding the strain relief mechanisms and their influence on the film morphology is therefore of primary importance.

As well as the interest in the Nb-Al₂O₃ interface because of the influence it exerts on superlattice structures, it is also of wider interest because metal-ceramic interfaces are in common use in many engineering materials [7], and as the interface influences device performance, fundamental studies on model systems to correlate the relationship between the microstructure and the properties are of significant interest. It is an excellent model system for such studies because Nb and Al₂O₃ possess similar thermal expansion coefficients and the thermodynamical properties of both materials are well understood. Furthermore no reaction products form at the Nb-Al₂O₃ interface.

This system has been the subject of extensive study, including x-ray diffraction analysis [8] and previous electron microscope examinations [9,10]. This chapter presents a combination of reflection high energy electron diffraction, RHEED, high resolution electron microscopy, HREM, and conventional transmission electron microscopy, CTEM, studies of the (110)_{Nb} || (11 $\bar{2}$ 0)_{Al₂O₃} interface, with the aim of characterising the coherent regions of the interface and uniquely identifying the nature of the misfit dislocations. RHEED has been used previously by Oderno et al. [11] to study the initial growth of niobium on sapphire. In common with their results it was found that the niobium initially grows with a hexagonal surface symmetry; however, this work also reports the observation of intensity oscillations in the RHEED specular beam during the subsequent growth of bcc niobium which was not

reported by Oderso et al. Previous work by Gutekunst et al. [10] with HREM on this interface has identified two possible consistent dislocation networks, but without the complementary use of CTEM they were unable to distinguish uniquely the correct network. However, detailed CTEM results on the misfit dislocations have been reported by Tricker and Stobbs [12], and the results of both groups will be discussed in the context of the present work.

5.1.1 Crystallography

It has been emphasised by previous authors [13,14] that the Nb/Al₂O₃ epitaxy is a unique three-dimensional relationship between the niobium and the sapphire, and the orientation relationships at the (110)_{Nb} || (11 $\bar{2}$ 0)_{Al₂O₃} interface are such that in the plane of the interface the 3-fold axes in the two structures are aligned, with $[\bar{1}\bar{1}1]_{\text{Nb}} || [0001]_{\text{Al}_2\text{O}_3}$. An untwinned Nb crystal layer forms with $[\bar{1}\bar{1}\bar{2}]_{\text{Nb}} || [\bar{1}\bar{1}00]_{\text{Al}_2\text{O}_3}$, as discussed in section 3.2.

It is worth noting that factors such as lattice mismatch and twinning mechanisms are different for the various sapphire orientations and so the crystalline quality of the Nb can also vary and each sapphire/niobium orientation must be considered separately. The fact that there does exist a unique 3-dimensional relationship between the Nb and the Al₂O₃ means that the Nb can be regarded as an extension of the Al sub-lattice of sapphire.

Two separate approaches to the calculation of critical thickness are outlined in section 3.3. The theory assumes that below a certain layer thickness, known as the critical thickness (h_c), the metal layer is homogeneously strained into registry with the substrate in the interfacial plane. It can distort tetragonally in the perpendicular direction in order to preserve the volume of the unit cell. There is an elastic strain energy associated with the epilayer (due to the tetragonal distortion) which increases with film thickness until at the critical thickness, $h=h_c$, it is energetically unfavourable to deposit additional layers in

registry with the substrate and so the strain is partially relieved by the introduction of misfit dislocations. As the film thickness increases further the dislocation density increases until the average strain is eventually reduced to zero, and the film has relaxed to its bulk lattice parameters. A dislocation network is required for a complete accommodation of the two-dimensional lattice mismatch. It should be emphasised that the mismatches are large in Nb/Al₂O₃ (1.9% and 12% respectively perpendicular and parallel to [0001]_{Al₂O₃}) and this combined with the fact that the crystal structures and bonding types of the two materials are different limits the applicability of simple theories. Nevertheless it is of interest to estimate the value of critical thickness in this system.

Equation 3.31, only valid for the case of a thin film on an infinitely thick substrate with an infinitely thick cap is the most applicable theory to the case of a thin film of niobium on sapphire. This gives the critical thickness at which it is energetically favourable for misfit dislocations to form as

$$h_c = \frac{b}{4\pi(1+\nu)\varepsilon} \ln \left| \frac{h_c}{b} + 1 \right| \quad (5.1)$$

where ε is the strain present in the system, b the magnitude of the Burgers vector and ν is the Poisson ratio.

Equation (5.1) gives the critical thickness of the niobium layer to be approximately 4.7 nm considering the lattice mismatch perpendicular to [0001]_{Al₂O₃} (i.e. $b=0.286$ nm, $\nu=0.4$ and $\varepsilon=0.197$).

5.1.2 Geometry of the Burgers vector of misfit dislocation

In comparison to bulk dislocations where Burgers vectors may be decomposed into an edge component and a screw component, for misfit dislocations it is more appropriate to decompose the vector into three components, two edge components $\underline{b}_{MD}$ and $\underline{b}_{\perp}$, and a

screw component $\underline{b}_{\text{screw}}$. $\underline{b}_{\text{MD}}$ is parallel to the interface and accommodates the lattice mismatch, whereas $\underline{b}_{\perp}$ is perpendicular to the interface and does not accommodate any lattice mismatch. The lattice would be tilted by a regular array of $\underline{b}_{\perp}$, and so if this Burgers vector exists in a network it must be compensated for in order to avoid this tilt. $\underline{b}_{\text{screw}}$ would twist the lattice of the film relative to the substrate.

If the lattice mismatch is entirely accommodated by the edge components, $\underline{b}_{\text{MD}}$, of

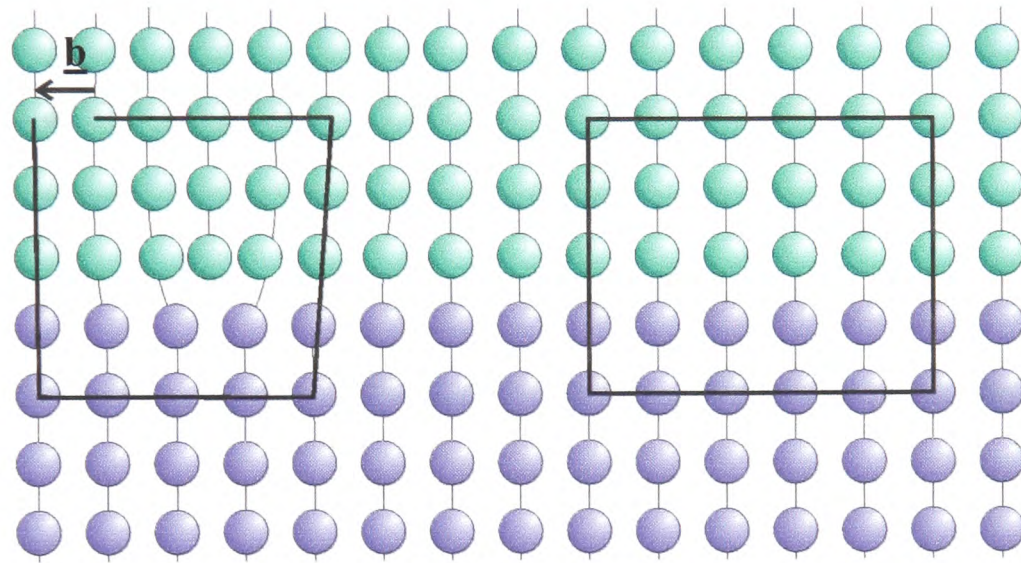


Figure 5.1: schematic diagram showing a Burgers circuit in a coherent region (right)

and a Burgers circuit around a misfit dislocation where the closure failure results in the
Burgers vector

the misfit dislocations so that there is no residual strain within the film, then the average distance between the misfit dislocations in a given direction is:

$$d_{\text{MD}} = \frac{|\underline{b}_{\text{MD}}|}{\delta} \quad (5.2)$$

where δ is the misfit accommodated by the dislocations, and from equation 3.32 it can be seen that when there is no residual strain δ equal to the lattice mismatch.

5.1.2.1 Method for determining the Burgers vector of a misfit dislocation

To determine the Burgers vector of a dislocation a ‘Burgers circuit’ is defined around the dislocation, and this is compared with a reference circuit in coherent regions [15] and the closure failure results in the Burgers vector, as shown in Figure 5.1. When the

dislocation occurs at the interface it is necessary for the Burgers circuit to cross the interface and thus a knowledge of the atomic structure of the interface is required.

5.2 Samples Analysed

The samples studied had a nominal thickness of niobium between 8nm and 50nm. The substrate temperature was held at 750°C during growth and the growth rate was 0.5nm/s of Nb. To study the initial growth of the niobium on sapphire in some cases the growth was interrupted for RHEED analysis after the deposition of 2, 4 and 6 monolayers respectively.

Specimens suitable for viewing the interfaces both in plan view and in cross-section were made by the techniques outlined in section 4.3. HREM has been used to identify the atomic structure of the coherent regions of the interface. Computer simulations, using the software package EMS [16], of a through-focal series using crystal models enabled accurate determination of the atomic structure of the coherent regions of the interface to be made. For the simulations geometric constructions of the two lattices have been used, as at present a model for the relaxed structures is not available. In the models, the Nb is strained in the interface plane according to the lattice mismatch, and the plane spacings of (110) planes are the bulk plane spacings of the metal. The displacement field of the misfit dislocations is not considered.

The plan view samples were characterised using TEM. The images were taken using weak beam diffraction conditions, because it is impossible to distinguish the contrast of a Moiré pattern and a dislocation network if the average distance between the misfit dislocations is smaller than $\frac{1}{3}\xi_g$ where ξ_g is the extinction distance for a particular Bragg reflection, $\mathbf{g}$ [17]. In bright field conditions $\xi_{110} = 26\text{nm}$, and so the misfit dislocation average spacings of 14nm and 2.5nm, as determined by equation 5.2, would not both be

distinguished. Images were taken in dark field at 50 000x, in selected area mode. With an excitation error $s_g=0.2\text{nm}^{-1}$, the effective extinction distance $\xi_{110\text{ eff}}$ is 5nm, and so it is possible to identify the dislocations.

5.3 Results and Discussion

5.3.1 RHEED results

Initially the RHEED beam is oriented along the $[0001]_{\text{Al}_2\text{O}_3}$ azimuth , as shown in 4.10(a), and the surface exhibits several Kikuchi lines. When the niobium begins to deposit the intensity of the Kikuchi lines decreases, and after the deposition of 0.5 nm of Nb, the RHEED pattern shows new lines, as shown in Figure 5.2(a). The lines are broad because the atoms are not well ordered on the surface. The pattern is coincident with the

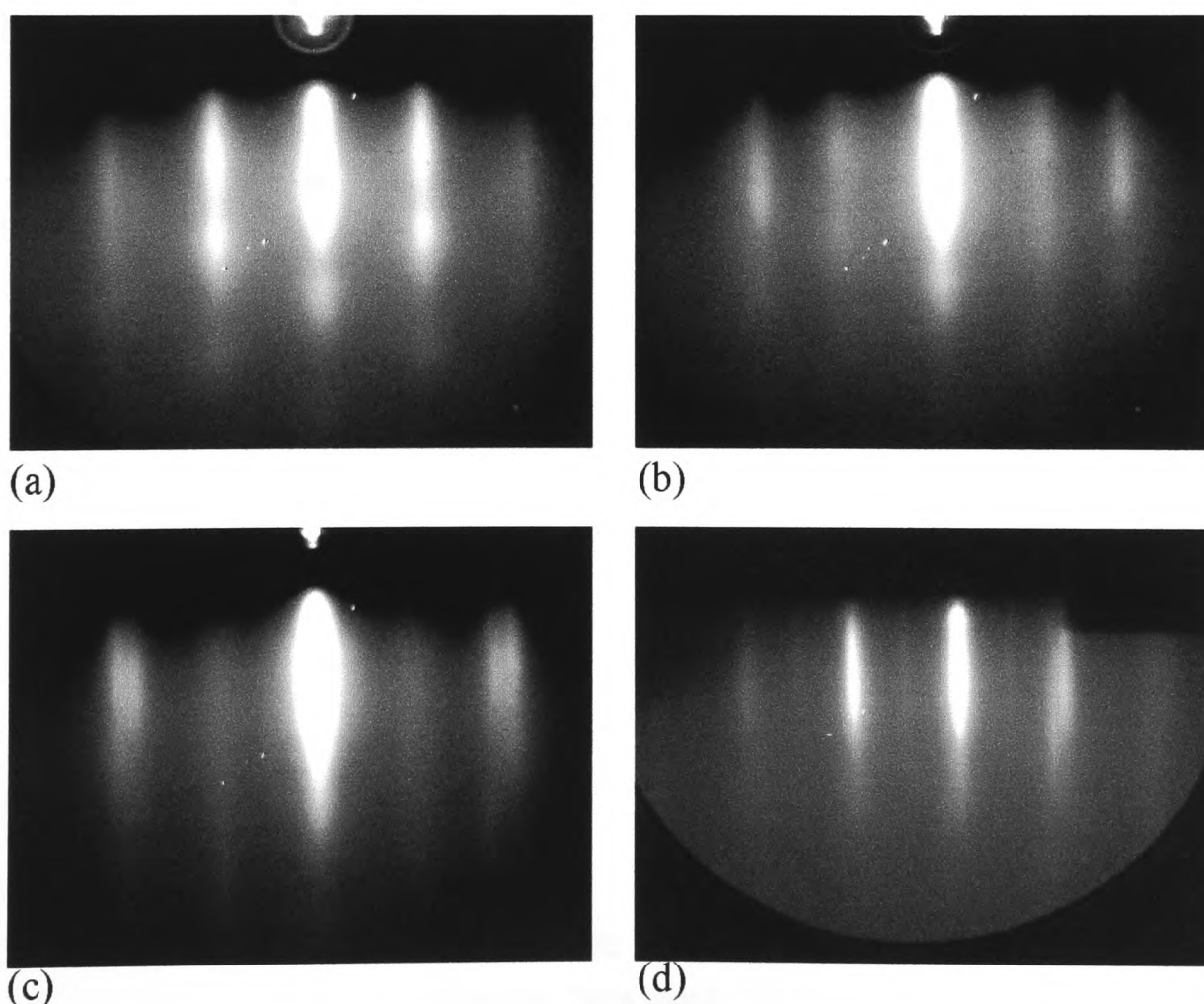


Figure 5.2: RHEED patterns from (a) Nb surface ($h = 5\text{\AA}$, where h - thickness of Nb layer) parallel to $[0001]_{\text{Al}_2\text{O}_3}$ (b) Nb surface ($h = 0.5\text{nm}$) parallel to $[\bar{1}100]_{\text{Al}_2\text{O}_3}$ (c) Nb surface ($h = 1\text{nm}$), both hexagonal and bcc lines are observed (d) Nb surface ($h = 1.5\text{ nm}$), only the bcc structure remains.

$[0001]_{\text{Al}_2\text{O}_3}$ azimuth and is found again when the sample is rotated by $\pm 60^\circ$ and $\pm 120^\circ$. The spacing of atomic rows parallel to the $[0001]_{\text{Al}_2\text{O}_3}$ direction was $2.66 \pm 0.11 \text{ \AA}$. A different line pattern was observed along $[\bar{1}100]_{\text{Al}_2\text{O}_3}$, also with 6-fold symmetry, with an atomic row spacing of $1.53 \pm 0.06 \text{ \AA}$, and is shown in Figure 5.2(b). The sixfold symmetry of the RHEED pattern combined with the $3^{1/2}$ ratio between the interline distances shows that the surface is hexagonal. When 0.5-1 nm of Nb has been deposited, as shown in Figure 5.2(c), the streaks coexist with those typical of a bcc Nb (110) structure, which can be seen in the figure by the splitting of the peaks. With 1.5 nm of Nb, Figure 5.2(d), the pattern revealed only the bcc Nb structure, with the epitaxy between the sapphire and the bcc Nb (110) being $[0001] \parallel [\bar{1}11]$ and $[\bar{1}100] \parallel [\bar{1}12]$. Similar results have been reported by Oderno et al. [11]. After the hexagonal structure has been superseded by the bcc Nb, the intensity in the specular beam is observed to oscillate. The intensity oscillations of the RHEED specular beam was monitored as a function of time for the growth of a thick layer of Nb ($h = 500 \text{ \AA}$). This is shown in Figure 5.3.

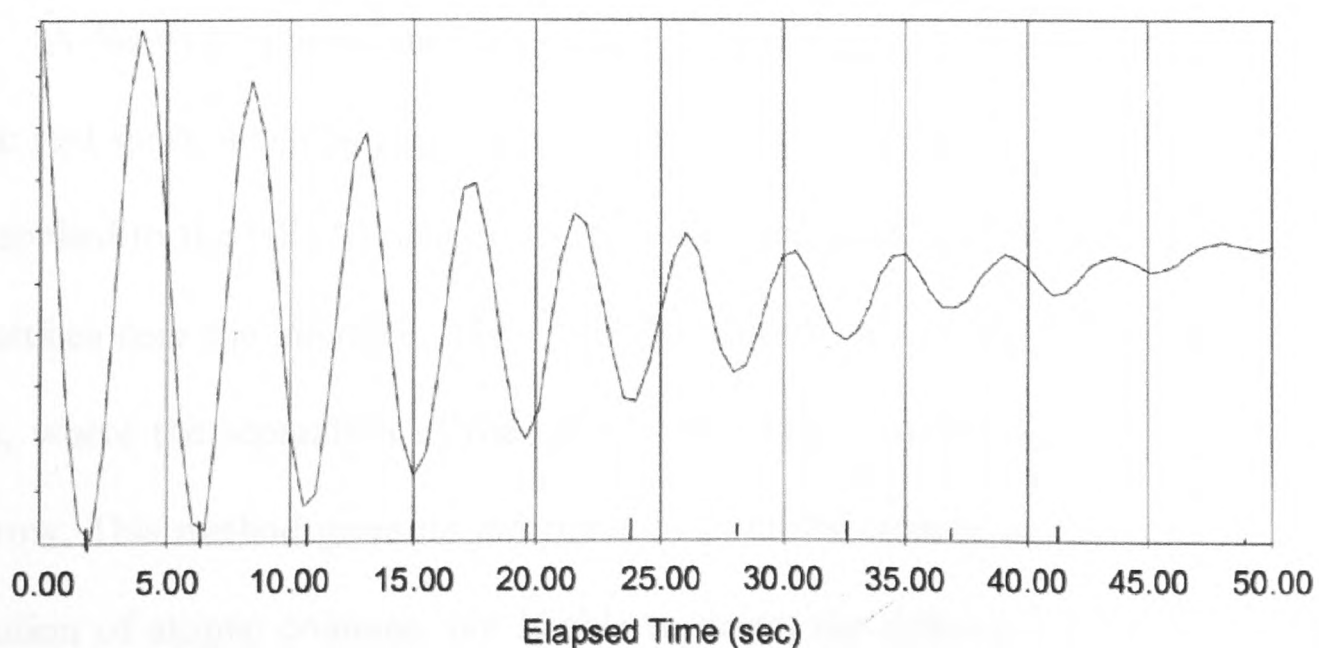


Figure 5.3: RHEED oscillations observed during the initial growth of bcc Nb

5.3.2 Electron Microscopy results

5.3.2.1 Coherent regions

HREM micrographs taken along $[\bar{1}\bar{1}\bar{1}]_{\text{Nb}} \parallel [0001]_{\text{Al}_2\text{O}_3}$ are shown in Figure 5.4, and have been evaluated by comparison with simulated images. The models used were proposed by Gutekunst et al. [9] who used a quantitative method to evaluate the closest match between simulated image and micrograph. The experimental images show that the $(011)_{\text{Nb}}$ and $(10\bar{1})_{\text{Nb}}$ planes transfer continuously into the $(\bar{1}210)_{\text{Al}_2\text{O}_3}$ and $(\bar{2}110)_{\text{Al}_2\text{O}_3}$ planes respectively. The model used for the simulations is shown in Figure 5.5. Unfortunately for this interface system it is not possible to simulate the interface along another direction, and thus build up a true 2-dimensional picture of the interface, as perpendicular to the $[\bar{1}\bar{1}00]_{\text{Al}_2\text{O}_3} \parallel [\bar{1}\bar{1}\bar{2}]_{\text{Nb}}$ direction it is necessary to resolve the $\{222\}_{\text{Nb}}$ planes ($=0.095\text{nm}$) which is below the resolution of the microscope. The nearest low index zone axis to the $[\bar{1}\bar{1}00]_{\text{Al}_2\text{O}_3} \parallel [\bar{1}\bar{1}\bar{2}]_{\text{Nb}}$ direction is $[4\bar{4}01]_{\text{Al}_2\text{O}_3} \parallel [\bar{1}\bar{1}\bar{1}]_{\text{Nb}}$, but the latter axes are not exactly parallel in this direction (2° rotation) and thus simulation is not possible.

A linewidth spectral analysis, which is essentially a 1-dimensional Fourier transform of the real space image applied row-by-row to give a spatially resolved spectral image [18], was applied to the HREM images, to study the coherency relation and strain field present in the lattices near the interface. The Fourier transform of a single atomic line forms a pair of spots, where the separation of the spots is inversely proportional to the atomic spacing in that row. This method gives no information about the content of unit cells or the individual relaxation of atomic columns, but is able to detect the difference between a hexagonal Nb surface structure, and a bcc Nb surface structure. The spectral image is shown in Figure 5.6 and reveals two important things about the $(110)_{\text{Nb}} \parallel (11\bar{2}0)_{\text{Al}_2\text{O}_3}$ interface. Firstly that for

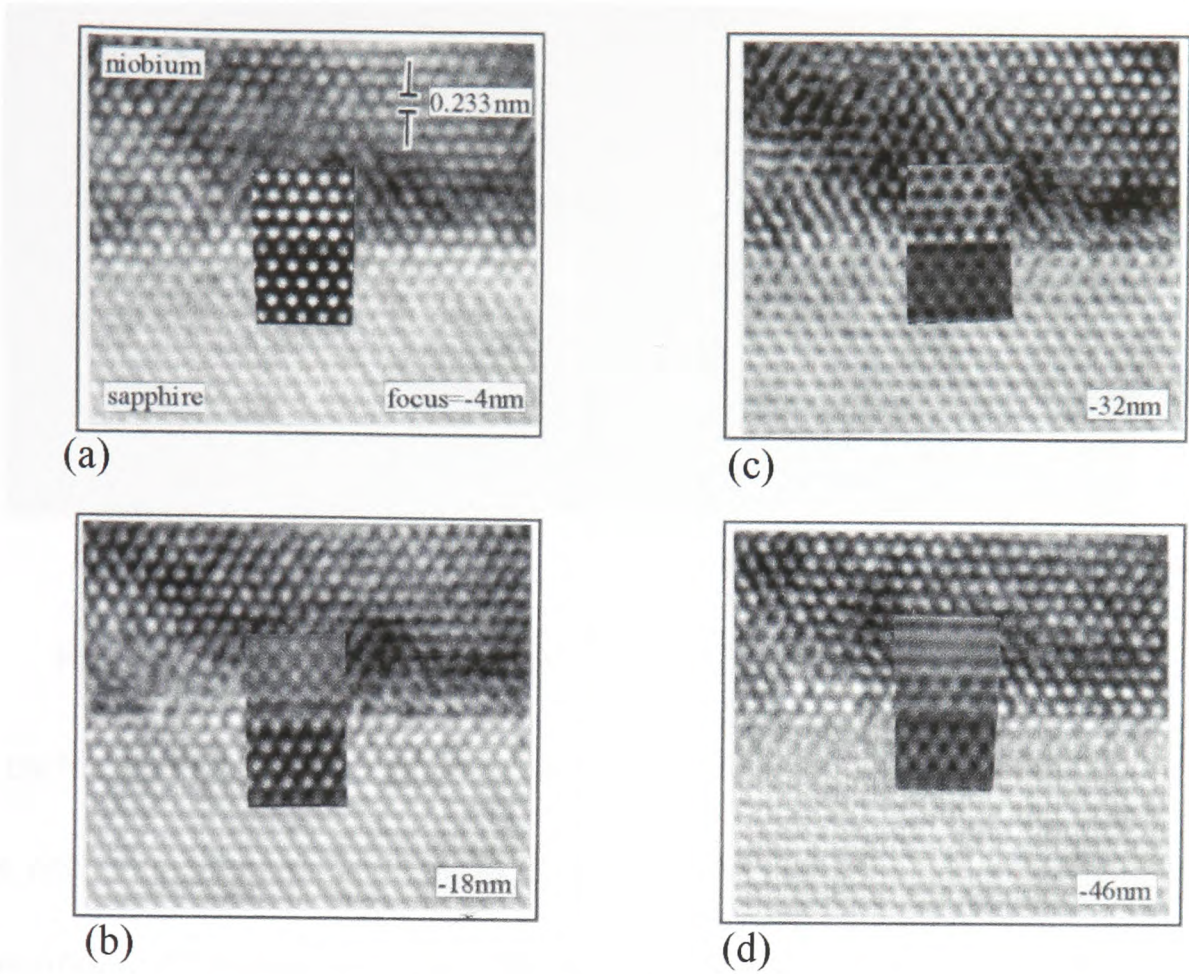


Figure 5.4: A through focal series of the (110)_{Nb} || (11̄20)_{Al₂O₃} interface imaged along $[1\bar{1}1]_{\text{Nb}} \parallel [0001]_{\text{Al}_2\text{O}_3}$

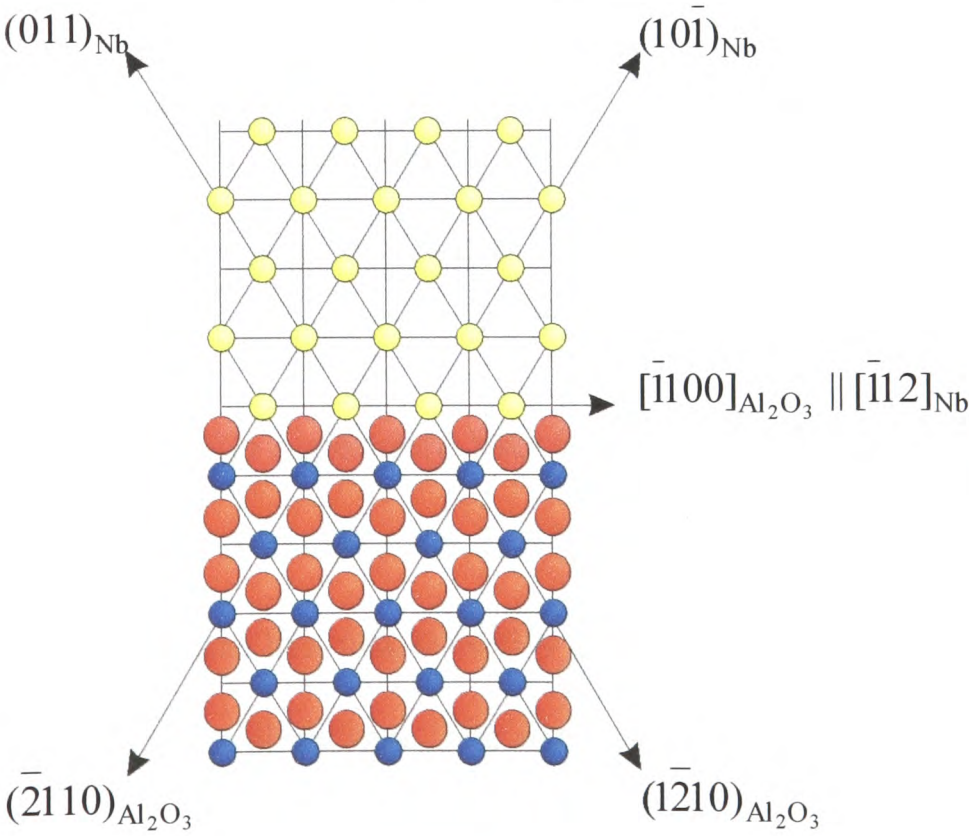


Figure 5.5: the atomic structure of the (110)_{Nb} || (11̄20)_{Al₂O₃} interface

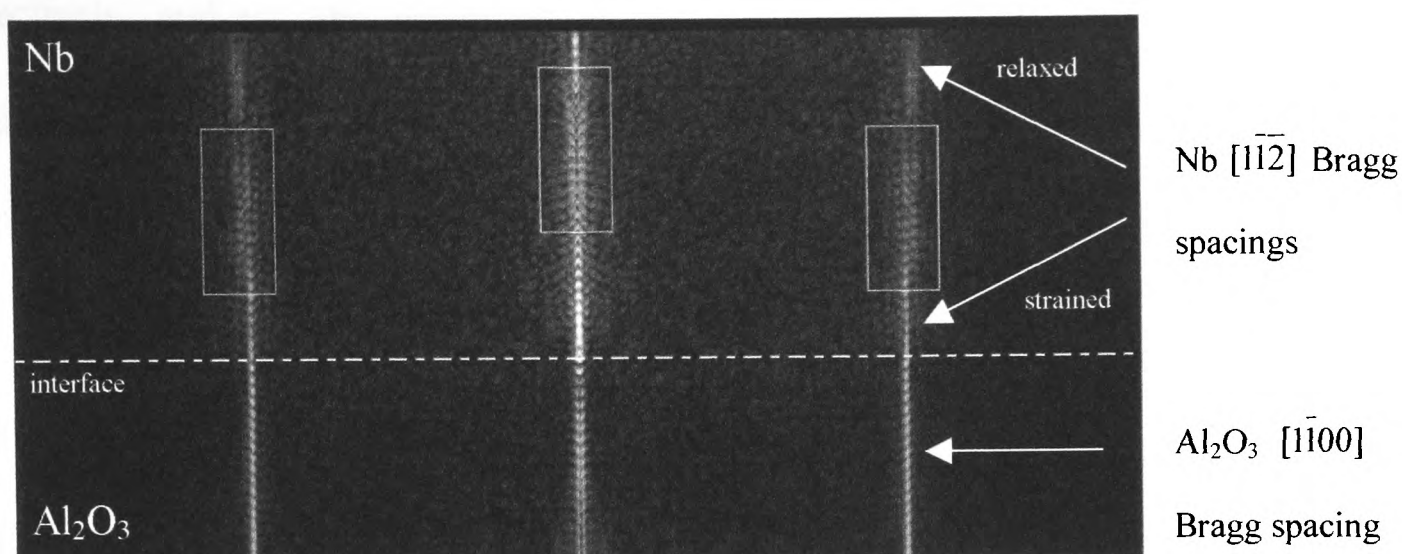


Figure 5.6: linewise spectral analysis of $(110)_{\text{Nb}} \parallel (11\bar{2}0)_{\text{Al}_2\text{O}_3}$ interface

"thick" niobium films (i.e. thicker than a few monolayers) no trace of the hexagonal structure remains. Thus as the system relaxes to bcc this is realised throughout the whole Nb layer. Secondly, it can be seen that the Nb lattice is strained to the sapphire sublattice. An extra reflection at $\sim 1/50$ th of the horizontal lattice period occurs over a small region ($\sim 5/6$ atomic planes) on the z-axis (inner box). This superstructure periodicity goes along with an overlap of the fundamental frequencies of the two bulk lattices (outer boxes). The latter observation implies that there is a dislocation network, but that it extends over several atomic layers normal to the interface. This network is studied in more detail in section 5.3.2.2.

The observation of RHEED oscillations indicates that the growth in the initial stages, is 2-dimensional, as discussed in section 4.2.2. The growth rate of the sample can be extracted from the oscillations and this rate confirms the proscribed growth rate of $0.5 \text{ \AA s}^{-1}$, which is set during pre-growth calibrations. The oscillations persist over approximately 20 monolayers until they are no longer detectable. The decay in peak intensity reflects a gradual increase in surface roughness. For FM growth to be sustained over several monolayers $\gamma_{\text{Nb}} < \gamma_{\text{S}}$, where $\gamma_{\text{Nb}} < \gamma_{\text{S}}$ are the surface free energies of niobium and sapphire

respectively, and γ_{in} , the interfacial strain energy, is initially small enough so that the inequality (equation (3.2));

$$\begin{aligned} (\gamma_f + \gamma_i - \gamma_s)_n &\leq 0 & \text{for } n < n^* \\ &> 0 & \text{for } n \geq n^* \end{aligned}$$

is satisfied. When $n \approx 20$ monolayers have been deposited, γ_{in} becomes sufficiently large that FM growth is no longer sustainable, and 3D clusters begin to form on the surface.

It is clear from the RHEED results that the first two monolayers of niobium deposited on sapphire do not show the expected (110) bcc Nb plane, which has rectangular symmetry, but instead a structure with hexagonal symmetry. Although the (111)_{Nb} plane would also exhibit 6-fold symmetry, the measured hexagonal surface spacing of 0.307 ± 0.012 nm does not agree with the interatomic distances of the (111)_{Nb} plane, which is 0.47 nm along the $[\bar{1}10]$ direction.

Figure 5.7 shows the relationship between the hexagonal Nb and sapphire planes.

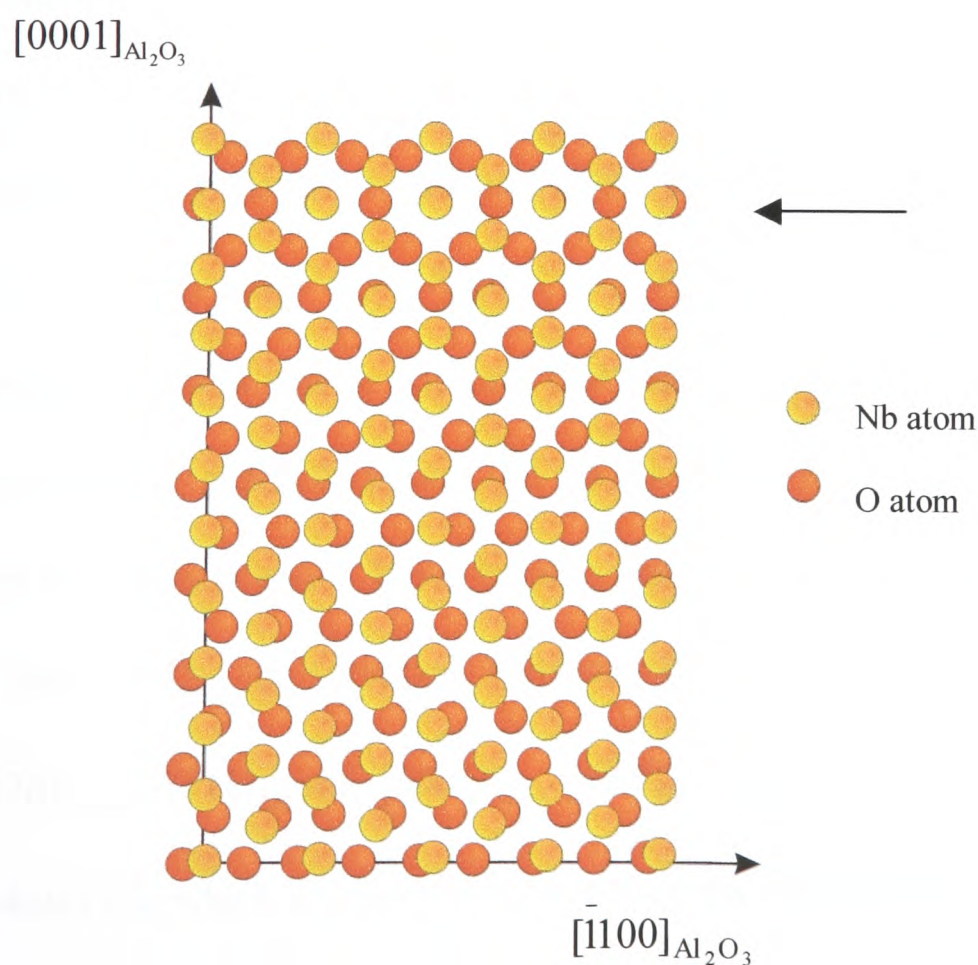
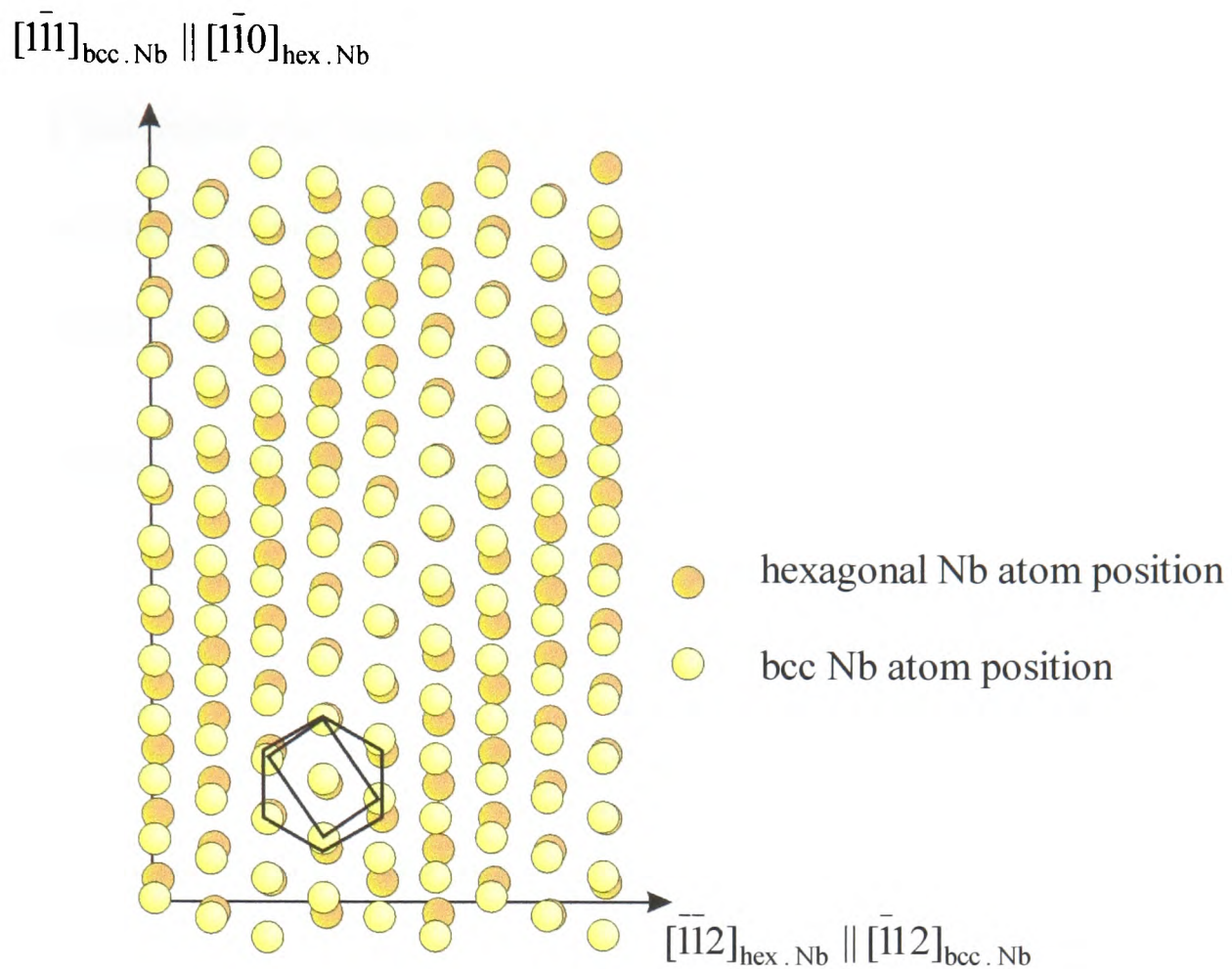


Figure 5.7: Nb-O bonding in the sapphire-niobium interface

The interface shows regions of small misfit, or good matching, as indicated with the arrow but with intervening areas where the misfit between the two structures is large. Initially it seems surprising that this structure is adopted. However in the sapphire lattice the rows of oxygen atoms are corrugated perpendicular to the [0001] direction, and it is probably this corrugation that enables a hexagonal surface structure to be viable. The question remains as to why the structure forms in hexagonal symmetry. It is postulated that the Nb overgrowth is governed by Nb-O bonds at the interface, and the resulting hexagonal plane is a compromise between the Nb trying to adopt the Al positions in the sapphire sublattice and the structure trying to adopt a form of Nb-O bonding. The hexagonal structure has a lower mismatch along [0001]_s of only 8% between the sapphire and hexagonal niobium compared with 13.6% in the case of bcc niobium. The ideal stoichiometry between the oxygen termination plane and the niobium would be Nb₂O₃. However the only known Nb-oxide species are Nb₂O₅, NbO₂ and NbO. From the observed structure it seems that it is the NbO structure that is adopted. The structure was observed by Petrucci et al. [19] during the growth of thin film niobium and niobium oxide on sapphire and is defined as NbO-6C and. It has a cubic structure and lattice parameter $a_0=4.21\text{\AA}$ with the NaCl type atomic configuration, but the vacancies are ordered at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ so that the number of formula units per unit cell, $Z=3$. The x-ray work of Petrucci et al. revealed the oxide to have an fcc structure which they hypothesised was due to the fact that during growth there is a random distribution of Nb atoms on the available lattice and vacancy sites leading to a statistical 75% occupancy of each fcc Nb lattice site. If we assume that the observed hexagonal NbO surface structure is in fact NbO, the epitaxy between the fcc Nb and the sapphire is defined by $(11\bar{2}0)_{\text{Al}_2\text{O}_3} \parallel (111)_{\text{Nb}}$ and $[0001]_{\text{Al}_2\text{O}_3} \parallel [\bar{1}\bar{1}0]_{\text{Nb}}$, and the corresponding fcc lattice parameter is $4.34\pm 0.18\text{\AA}$, which is comparable with the bulk NbO lattice parameter.

Figure 5.8: schematic diagram of the $\alpha(\text{hcp}) \rightarrow \beta(\text{bcc})$ transition

It is observed that after the deposition of the first few monolayers the Nb-O bonds cease to dominate the epitaxy and the structure reverts to its bulk bcc lattice. This transition from the hexagonal surface structure to the cubic structure is of great interest. Although the initial growth prefers a hexagonal surface structure, it seems that when there is a sufficient thickness of Nb deposited ($\sim 0.5\text{-}1$ nm) the energy of the system is minimised by relaxing to its bulk bcc structure, because the energy required to add additional atoms in hexagonal sites is just too high. This hexagonal $\rightarrow$ bcc transition is realised with a shear along the $[110]_{\text{Nb}}$ direction as shown in Figure 5.8. As the 1-dimensional Fourier transform of the interface reveals no trace of the fcc structure with only the bcc structure remaining, it appears that the whole Nb layer relaxes.

In bulk materials, six equivalent hexagonal $\rightarrow$ bcc transitions are possible. However in niobium films grown on sapphire substrates, only one bcc orientation relative to the

sapphire lattice is observed. The sapphire surface lattice breaks the symmetry of the system and therefore influences the transition. As HREM work has shown [9,20] in thicker Nb films (i.e. films that have undergone the hexagonal $\rightarrow$ bcc transition) the niobium atoms are as close as possible to the sites of a continued aluminium sublattice of sapphire.

5.3.2.2 Incoherent regions – Misfit Dislocations

The niobium lattice is strained in two dimensions to match the lattice of the substrate. Therefore at least two arrays of misfit dislocations are needed to accommodate the lattice mismatch, and HREM images have to be taken in at least two different orientations to image the misfit dislocations of a network. HREM images of the $(11\bar{2}0)_{\text{Al}_2\text{O}_3} \parallel (110)_{\text{Nb}}$ interface have been taken along the projections $[0001]_{\text{Al}_2\text{O}_3} \parallel [\bar{1}\bar{1}\bar{1}]_{\text{Nb}}$, Z1 in Figure 5.9, and $[\bar{4}\bar{4}01]_{\text{Al}_2\text{O}_3} \parallel [\bar{1}\bar{1}\bar{1}]_{\text{Nb}}$, Z2 in 5.9. The Al_2O_3 -Nb interface has been shown by Gutekunst [9] to be semicoherent above the critical thickness.

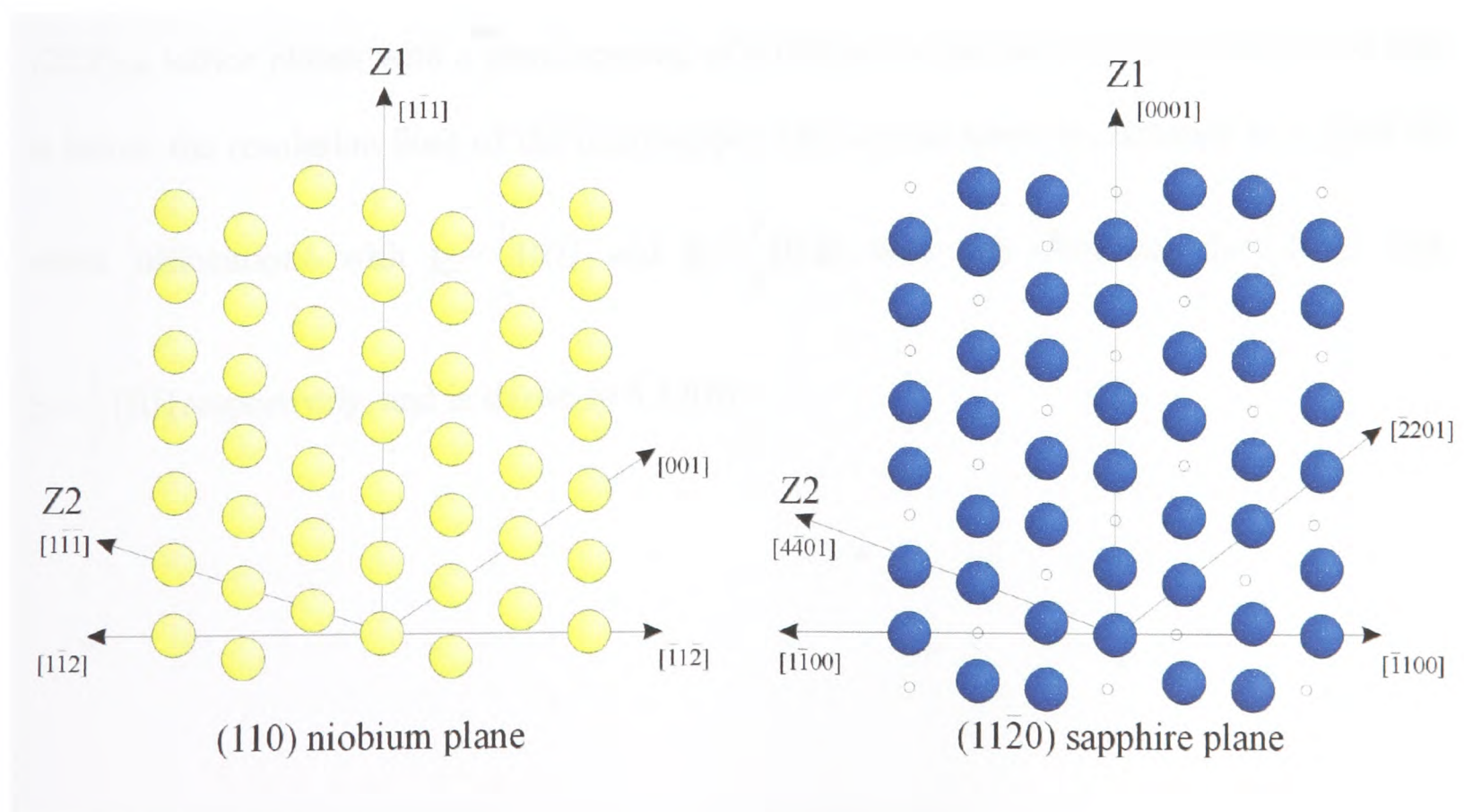


Figure 5.9: Plan view relationship of the $(110)_{\text{Nb}} \parallel (11\bar{2}0)_{\text{Al}_2\text{O}_3}$ interface

Misfit dislocations were identified both with and without stand-off, i.e. displaced from and located at the interface. 5.10(a) shows a misfit dislocation without stand-off. The misfit dislocation in Figure 5.10(b) has a stand-off of approximately 5 (110)_{Nb} planes. The projected Burgers vector along Z1 determined from the HREM image is $\frac{1}{3}[\bar{1}12]$. Another set of misfit dislocations were imaged along Z2 (Figures 5.11(a) and 5.11(b)). The projected Burgers vector was determined to be $\frac{1}{3}[\bar{1}1\bar{2}]$. There are two networks that are consistent with the experimental data. Both networks consist of pure edge dislocations with the Burgers vector parallel to the interface plane. Network A is built of misfit dislocations with $\underline{\mathbf{b}}_1 = \frac{1}{2}[\bar{1}11]$ and $\underline{\mathbf{b}}_2 = \frac{1}{2}[\bar{1}\bar{1}1]$, with line directions $\xi_1 = \frac{1}{3}[\bar{1}1\bar{2}]$ and $\xi_2 = \frac{1}{3}[\bar{1}12]$ respectively and is shown in Figure 5.12(a). The line directions are not parallel to Z1 and Z2, in fact Z2 is rotated by 19.5° from the line direction. Thus we are not imaging the dislocations edge on, but at an angle. To image these dislocations edge on, i.e. along the $\langle 112 \rangle$ zone axis, the $\{222\}_{\text{Nb}}$ lattice planes with a plane spacing of 0.095nm would have to be resolved, and this is below the resolution limit of the microscope. The second network, network B, is built of misfit dislocations with $\underline{\mathbf{b}}_2 = \frac{1}{2}[\bar{1}\bar{1}1]$ and $\underline{\mathbf{b}}_3 = \frac{1}{3}[\bar{1}12]$ with line directions $\xi_2 = \frac{1}{3}[\bar{1}12]$ and $\xi_3 = \frac{1}{2}[\bar{1}\bar{1}1]$ respectively, and is shown in 5.12(b).

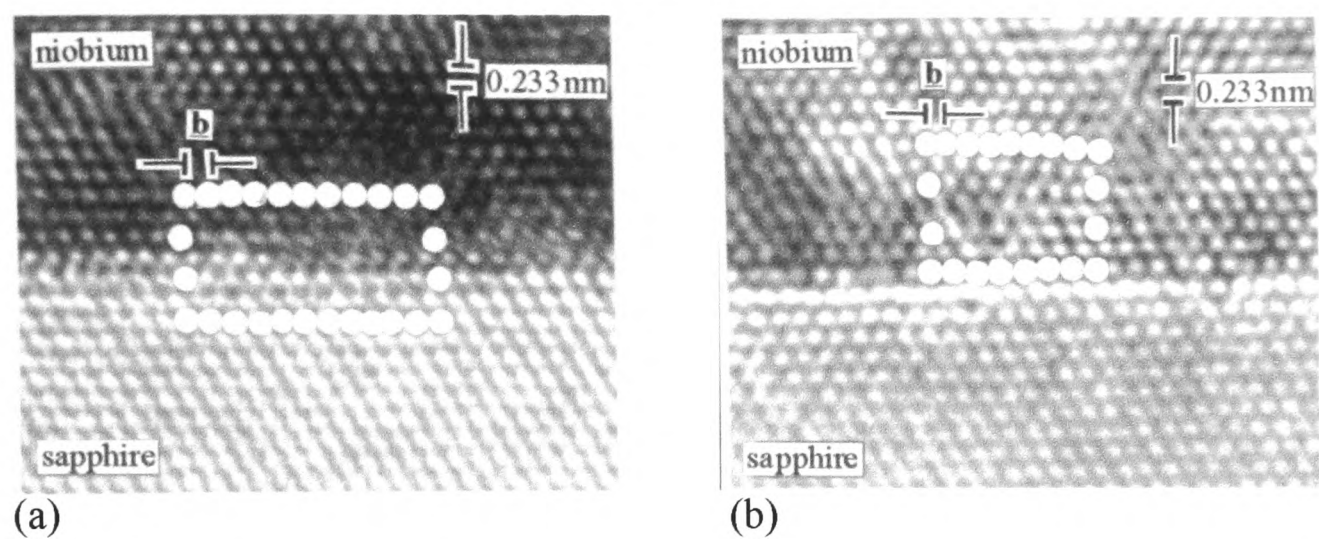


Figure 5.10: (a) misfit dislocation without 'stand-off' imaged along Z1, (b) Misfit dislocation with 'stand-off' imaged along Z1

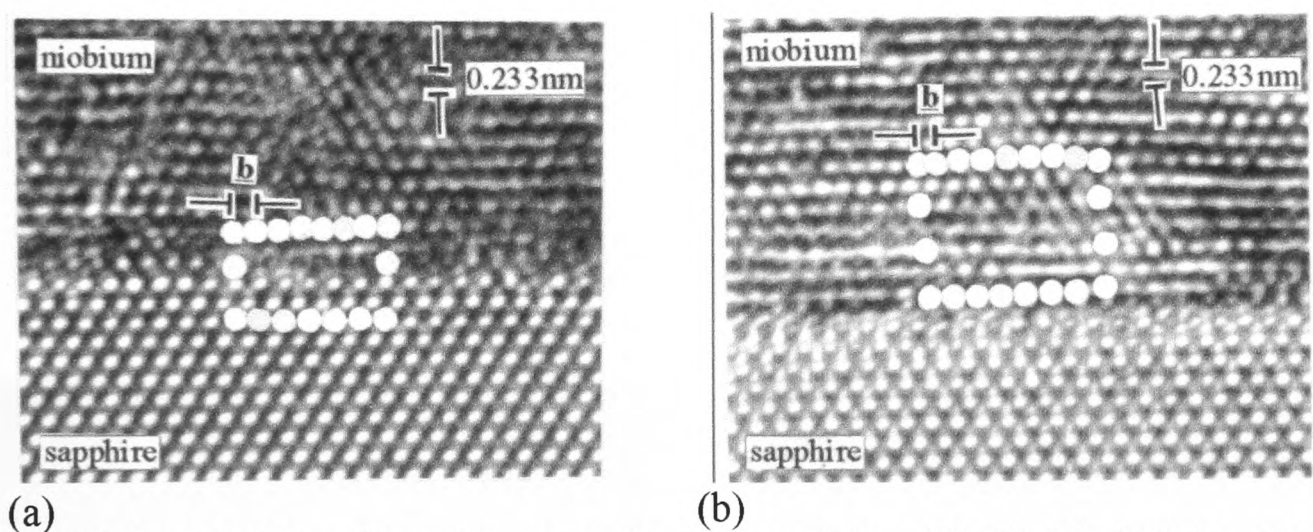


Figure 5.11: (a) misfit dislocation without 'stand-off' imaged along Z2, (b) Misfit dislocation with 'stand-off' imaged along Z2

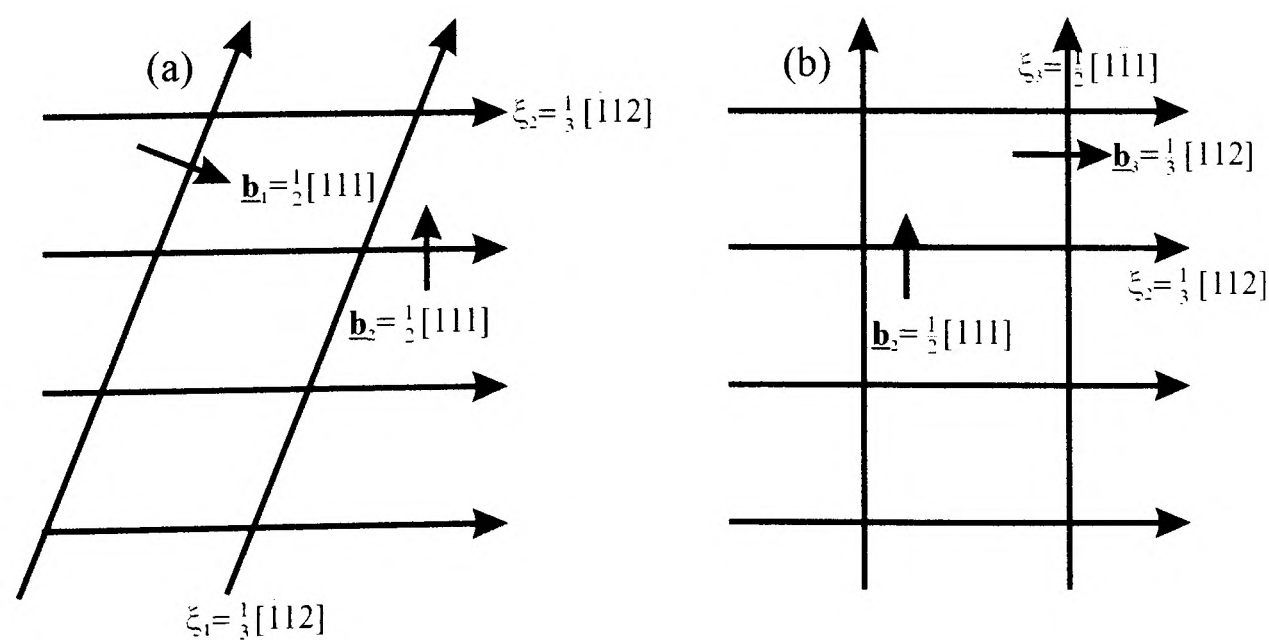
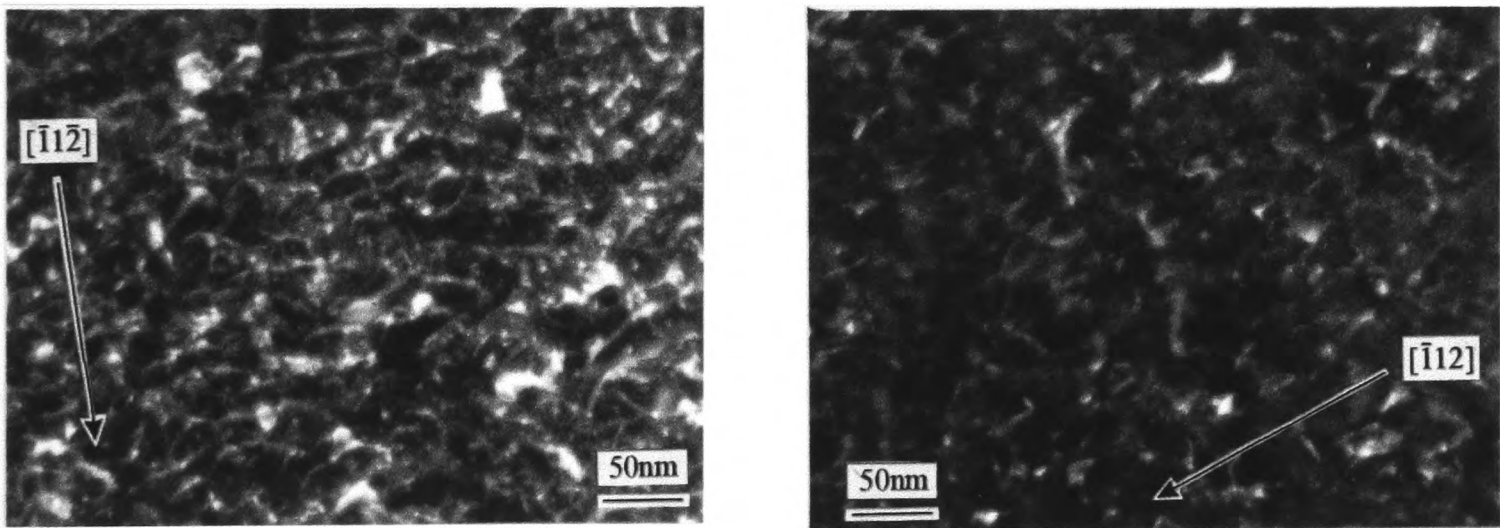


Figure 5.12: the two possible networks as determined by HREM, where $\underline{b}_1$, $\underline{b}_2$, $\underline{b}_3$ are the Burgers vector of the dislocations with respective line directions ξ_1 , ξ_2 and ξ_3 .

As HREM is not able to determine the line directions of the dislocations, we have used conventional TEM to determine the correct network. Weak-beam images of the niobium/sapphire interface in plan view were taken to enable the use of conventional $\mathbf{g} \cdot \mathbf{b}$ and $\mathbf{g} \cdot \mathbf{b} \times \mathbf{u}$ analysis, shown in Table I, to distinguish which is the actual network. The images shown in Figures 5.13(a) & 5.13(b) reveal the network to be somewhat irregular, with dislocations not generally straight.

$\mathbf{b}$	$\mathbf{g}$	$[\bar{1}12]$	$[1\bar{1}2]$	$[002]$
$\mathbf{b}_1 = \frac{1}{2}[\bar{1}11]$		x	0	x
$\mathbf{b}_2 = \frac{1}{2}[1\bar{1}1]$		0	x	x
$\mathbf{b}_3 = \frac{1}{3}[\bar{1}12]$		x	x	x

Table 5.1: $\mathbf{g} \cdot \mathbf{b}$ analysis for CTEM experiment



(a) (b)
Figure 5.13: (a)CTEM plan view image of $(110)_{\text{Nb}} \parallel (11\bar{2}0)_{\text{Al}_2\text{O}_3}$ interface with $\mathbf{g}=[\bar{1}1\bar{2}]$ (b)

CTEM plan view image of $(110)_{\text{Nb}} \parallel (11\bar{2}0)_{\text{Al}_2\text{O}_3}$ interface with $\mathbf{g}=[\bar{1}1\bar{2}]$

Comparing Figures 5.13(a) and 5.13(b), it is clear that in Figure 5.13(b) the majority of dislocations are out of contrast, that is $\mathbf{g} \cdot \mathbf{b} = 0$. With $\mathbf{g} = [\bar{1}1\bar{2}]$ this implies that $\mathbf{b} = \frac{1}{2}[\bar{1}11]$. It follows that the Burgers vector of the majority of the dislocations shown in Figure 5.13(a) is

$\underline{\mathbf{b}} = \frac{1}{2}[\bar{1}\bar{1}1]$. Referring to Figure 5.13(a), it can be seen that $\underline{\mathbf{b}} = \frac{1}{2}[\bar{1}\bar{1}1]$ is perpendicular to the line direction of the dislocations imaged, and so we can conclude that the dislocations are mainly edge in character. The dislocations shown in Figure 5.13(b) by similar arguments must have $\underline{\mathbf{b}} = \frac{1}{2}[\bar{1}11]$. Thus the images appear to be consistent with network A.

In network A, the projected Burgers vector that is observed when viewing along Z1 can have a component that contributes to the Burgers vector that is observed when viewing along Z2. So the Burgers vector can be split into two partials

$$\frac{1}{2}[\bar{1}11] = \frac{1}{6}[\bar{1}\bar{1}\bar{1}] + \frac{1}{3}[\bar{1}12] \quad (5.3)$$

$$= \underline{\mathbf{b}}_{\text{MD1}} + \underline{\mathbf{b}}_{\text{MD2}}. \quad (5.4)$$

The mismatch taken up along $\underline{\mathbf{b}}_{\text{MD2}}$ is 1.97%, so the spacing between misfit dislocations is

$$d_{\text{MD}} = \frac{\underline{\mathbf{b}}_{\text{MD}}}{\delta_S} \approx 14 \text{ nm}. \quad (5.5)$$

Thus the average spacing of these dislocations from equation (5.5) should be 14nm. The irregular network and low density of dislocations of this type together with the residual contrast from $\frac{1}{2}\langle\bar{1}\bar{1}1\rangle$ make this prediction hard to verify.

The lattice mismatch parallel to the $[\bar{1}\bar{1}1]$ direction is 12%. This is accommodated by misfit dislocations in the line directions ξ_1 and ξ_2 . Along ξ_2 misfit dislocations occur every 14nm, so;

$$d_{\text{MD}} = \frac{\underline{\mathbf{b}}_{\text{MD}}}{\delta_{S_{\text{eff}}}} \quad (5.6)$$

where $\delta_{S_{\text{eff}}}$ is the amount of misfit accounted for by dislocations in this line direction. By

rearranging equation (5.6) and substituting from equation (5.5) it can be seen that;

$$\delta_{S_{eff}} = \frac{1/2[\bar{1}\bar{1}1]}{14 \text{ nm}} \approx 0.6\% \quad (5.7)$$

Therefore, of the total 12% misfit, 11.4% must be accommodated for the misfit dislocations in the line direction ξ_1 , and so the spacing of misfit dislocations in this direction is;

$$d_{MD} = \frac{1/2[\bar{1}\bar{1}\bar{1}]}{0.114} \approx 2.5 \text{ nm} \quad (5.8)$$

The spacing of the the misfit dislocations from $\underline{b}_2$ will be a projection through an angle 19.5° , and so the effective dislocation spacing is 2.0nm. Figure 5.13(a) shows a spacing of $2.1 \text{ nm} \pm 10\%$.

This interface has also been studied using CTEM by Tricker and Stobbs [12] but they report a quite different network. Their results led to the conclusion that the dislocation network accommodates the lattice mismatch in the $[\bar{1}12]$ direction by misfit dislocations, with the line direction rotated away from the $[\bar{1}\bar{1}1]$ direction by 9° toward $[\bar{1}\bar{1}\bar{2}]$ and that the interface in the $[\bar{1}\bar{1}1]$ direction is incoherent. Their CTEM studies also show a twist of the Nb lattice by 0.33° , which was not observed in this work. Their results are assumed to differ from the results reported here because of the different growth method that was used. The samples that they studied were grown by dc magnetron sputter deposition at a temperature of $650\text{-}840^\circ\text{C}$, and of thicknesses up to $1\mu\text{m}$. The plan view samples were also prepared by a different method [21]. For samples prepared under these conditions the results are quite different.

5.4 Conclusions

In-situ RHEED experiments on the growing surface of (110) Nb on (11 $\bar{2}$ 0) Al_2O_3 have revealed two unexpected results. Firstly for the (11 $\bar{2}$ 0) $_{\text{Al}_2\text{O}_3}$ || (110) $_{\text{Nb}}$ interface prepared

by MBE with the substrate temperature held at 750°C during growth and a growth rate of 0.5nm/s of Nb, the RHEED has shown that the initial Nb is deposited with hexagonal symmetry, and appears to form in a NbO fcc phase for the first 2 monolayers, but as more Nb is deposited the energy required to keep the structure in this hexagonal phase is too high, and thus it relaxes to the bulk bcc Nb structure. Secondly RHEED has shown that after relaxation to the bcc structure then the Nb grows monolayer by monolayer for approximately the first 20 planes of growth.

Complementary use of HREM and CTEM has uniquely identified for the first time that the dislocation network for the semicoherent (110)_{Nb} || (11 $\bar{2}$ 0)_{Al₂O₃} interface consists of pure edge dislocations, with the Burgers vectors parallel to the interface plane. The Burgers vectors of the dislocations are $\underline{b} = \frac{1}{2}[\bar{1}11]$ and $\underline{b} = \frac{1}{2}[\bar{1}\bar{1}1]$, with line directions $\frac{1}{3}[\bar{1}1\bar{2}]$ and $\frac{1}{3}[\bar{1}\bar{1}2]$ respectively. As these correspond to the Burgers vectors characteristic of bulk niobium, it implies that the misfit dislocations do not alter the atomic structure of the coherent regions.

References

- [1] S. M. Durbin, J. E. Cunningham, M. E. Mochel, and C. P. Flynn, *J. Phys. F: Met. Phys.* **11**, (1981).
- [2] J. Kwo, E. M. Gyorgy, D. B. McWhan, M. Hong, F. J. DiSalvo, C. Vettier, and J. E. Bower, *Phys. Rev. Lett.* **55**, 1402 (1985).
- [3] M. B. Salamon, S. Sinha, J. J. Rhyne, J. E. Cunningham, R. W. Erwin, J. Borchers, and C. P. Flynn, *Phys. Rev. Lett.* **56**, 259 (1986).
- [4] D. F. McMorro, D. Jehan, P. P. Swaddling, R. A. Cowley, R. C. C. Ward, M. R. Wells, and K. N. Clausen, *Phys. B* **192**, 150 (1993).

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- [5] P. Bodeker, A. Abrometi, K. Bohl, P. Sonntag, N. Metoki, and H. Zabel, *Phys. Rev. B* **47**, 2353 (1993).
- [6] V. Oderno, C. Dufour, K. Dumesnil, P. Mangin, and G. Marchal, *J. Cryst. Growth* **165**, 175 (1996).
- [7] *Metal-Ceramic Interfaces; Vol.*, edited by M. Ruhle, A. G. Evans, M. F. Ashby, and J. P. Hirth Pergamon Press, New York, 1990.
- [8] A. R. Wildes, R. A. Cowley, R. C. C. Ward, M. R. Wells, C. Jansen, L. Wiren, and J. P. Hill, *J. Phys. C* **10**, L631 (1998).
- [9] G. Gutekunst, J. Mayer, and M. Ruhle, *Phil. Mag. A* **75**, 1329 (1997).
- [10] G. Gutekunst, J. Mayer, V. Vitek, and M. Ruhle, *Phil. Mag. A* **75**, 1357 (1997).
- [11] V. Oderno, C. Dufour, K. Dumesnil, A. Mougin, P. Mangin, and G. Marchal, *Phil. Mag. lett.* **78**, 419 (1998).
- [12] D. M. Tricker and W. M. Stobbs, *Phil. Mag. A* **71**, 1037 (1995).
- [13] J. Mayer, C. P. Flynn, and M. Ruhle, *Ultramicroscopy* **33**, 51 (1990).
- [14] A. Gibaud, R. A. Cowley, D. F. McMorrow, R. C. C. Ward, and M. R. Wells, *Phys. Rev. B* **48**, 14463 (1993).
- [15] J. P. Hirth and J. Lothe *Theory of Dislocations*, Wiley, New York, (1982).
- [16] P. A. Stadelman, *Ultramicroscopy* **21**, 131 (1987).
- [17] A. R. Tholen, *Phys. Stat. Sol. (a)* **2**, 537 (1970).
- [18] G. Mobus, E. Schumann, G. Dehm, and M. Ruhle, *Phys. Stat. Sol. (a)* **150**, 77 (1995).
- [19] M. Petrucci, C. W. Pitt, and S. R. Reynolds, *Appl. Phys.* **63**, (1988).
- [20] E. J. Grier, M. L. Jenkins, A. K. Petford-Long, R. C. C. Ward, and M. R. Wells, *Thin Solid Films* **358**, 94 (2000).
- [21] S. B. Newcomb, C. B. Boothroyd, and W. M. Stobbs, *J. Mic.* **140**, 195 (1985).

Chapter 6

Microstructural characterisation of rare earth (R=Ho,Y) based films

Chapter 6 presents the results of high resolution electron microscopy on rare earth (holmium, yttrium) metals and hydrides. The introduction (section 6.1) discusses previous results of high resolution electron microscope examinations of rare earth thin films grown by sputter deposition. There have been no reported examinations of epitaxial rare earth metal films grown by MBE on sapphire substrates. Section 6.2 reports the first successful preparation technique for epitaxial rare earth metal films. Section 6.3.1 presents the results of an investigation into such systems, examining the image contrast, the strain relief mechanisms and the limitations on making α -phase specimens by such a method. Sections 6.3.2 and 6.3.3 present the results of electron microscopy of specimens of rare earth hydrides.

6.1 Introduction

There has been very little electron microscopy performed on rare earth metal films, presumably because of their extreme reactivity and the associated difficulties with producing good specimens representative of the bulk. However some previous studies have

been carried out. Petford-Long *et al.* [1] reported the results of an HREM investigation of Gd/W multilayer films grown on [001] surface normal oxidised silicon wafers by DC magnetron sputter deposition in a UHV vacuum system. The specimens for microscopy were prepared by the method of Bravman and Sinclair [2] appropriate for the preparation of TEM specimens of metal films on silicon substrates. Their results showed that the Gd layers contained crystallites with a high degree of crystallographic texture, with the (0002) Gd planes lying parallel to the film plane. They also observed larger crystallites within the layers, which exhibited a face-centred cubic structure which was uniquely identified as GdH₂. The presence of fcc TbH₂ crystals has also been observed in electron microscopical characterisation of Tb/Fe multilayers by Cherifi *et al.* [3]. Cherifi *et al.* also state that they have observed a similar structure for Gd/Fe, Dy/Fe, Tm/Fe and Nd/Fe multilayers during routine TEM examination of specimens as part of a wider study into their transport and magnetic properties, although these results are not published. Both Petford-Long *et al.* and Cherifi *et al.* suggest that the crystallites form during the sputter deposition process, and Gasgnier [4] has pointed out that rare earths are excellent getters for hydrogen and that in rare earth films grown under high vacuum conditions (10^{-6} mbar) there is a very real possibility of forming the dihydride, RH₂. The dihydride forms by the metal reacting with water or residual hydrogen within the chamber. This process is hard to stop except by the efficient removal of all the water within the system.

6.2 Experimental details

The films studied in this chapter were grown by MBE, and a major advantage of MBE growth techniques for rare earth thin films, rather than sputter deposition, is that the source materials for MBE growth can be obtained with significantly higher purity than for sputter deposition, as no processing (i.e. rolling and shaping) is required, the environment is

ultra-high vacuum and it is also possible to outgas the source materials in-situ. This has enabled the growth of single crystal α -phase metals, as determined by XRD. However, it was observed that rare earth metal TEM specimens prepared by conventional specimen preparation techniques were all in the β -phase suggesting that the hydrogenation of MBE grown films was occurring during specimen preparation. Thus it was necessary to consider the specimen preparation techniques employed. The work of Petford-Long *et al.* [1] and Cherifi *et al.* [3] used preparation techniques appropriate for the preparation of TEM specimens from films grown on silicon substrates, which were different to those described in section 4.3.1 which details the conventional specimen preparation techniques employed in this thesis. An important difference between the preparation of specimens from films grown on silicon and from films grown on sapphire substrates is the time it takes to prepare a specimen. The coarse thinning and grinding stages can take a minimum of ~48 hours for specimens from films with a sapphire substrate compared with ~12 hours for specimens from films grown on a silicon substrate. The final thinning-to-perforation stage involves bombarding the TEM specimen with argon ions, which sputter material from the film until it is thin enough to be studied in the TEM. During this process the specimen is cooled to liquid-nitrogen temperatures to prevent mixing of the layers during thinning. Ion thinning is closely related to ion-beam deposition and so it is not surprising that similar effects, such as hydride formation, could occur during TEM specimen preparation. Although the chamber of the ion-beam thinning instrument is pumped with a turbomolecular pump, the background pressure is typically 5×10^{-6} mbar. Of the residual gases present in the chamber hydrogen and water vapour will form a significant fraction. Reaction with water vapour is made more likely by the necessity of cooling a specimen to liquid nitrogen temperature during thinning to prevent mixing of the layers, as the water vapour will condense on the specimen surface upon cooling. Although both TEM specimen preparation techniques involve the same

process the time involved for the different techniques was very different. For the Gd/W multilayers on Si substrates, using broad ion beam milling with an accelerating voltage of 6kV and current of 1mA, the time to perforation was typically of order 5-6 hours. This contrasts with a thinning time of order 50 hours for a rare earth film grown on a sapphire substrate. The reason for such a wide variance in thinning times is the different substrates. Sapphire thins much more slowly than silicon, and hence the milling time is increased. It is probably this difference in thinning time that enabled the preparation of metallic (in part) Gd/W multilayers and prevented the preparation of the rare earth films on sapphire substrates.

It has however proved possible to prepare metal specimens on sapphire substrates with a focused ion beam (FIB) system. The background pressure in the chamber is very similar to that of the broad ion beam chamber ($\sim 10^{-6}$ mbar) and so reduction of water by the metal vapour is still possible, but the main difference, as far as the formation of the hydrides is concerned, is the time that the process takes. The total time needed in the FIB system, using an accelerating voltage of 30 keV and currents from 100-1000 pA, is of order 2 hours. Other possibly significant differences are that in general FIB specimens are thicker and no cooling is required during preparation. The short preparation times means that even though the specimen surface may have formed the hydride, the bulk of the specimen remains in the metal phase. This is confirmed by the observation that there seemed to be an optimum thickness for FIB prepared specimens, in which the lattice fringes are resolvable, but the specimens are significantly thick, with the majority of the specimens still in the metallic state. Specimens that were thinner were observed to have formed the dihydride. Therefore a combination of the shorter preparation times, and the ability to keep specimens above a certain optimum thickness has enabled the observation of α -phase holmium and yttrium.

A 4000EX high-resolution electron microscope with a Scherzer resolution of 0.16nm was used to study the epitaxial thin films. The specimens were tilted in the microscope to align the [0001] direction of the sapphire substrate parallel to the electron beam. In this orientation the interfaces between the layers will also lie parallel to the electron beam, and can thus be viewed edge on. The $(11\bar{2}0)$ crystal lattice planes in the sapphire substrate were used as an internal calibration of magnification during subsequent analysis of the images obtained.

To determine the crystal structure, selected area electron diffraction, SAD, patterns were obtained from various areas of the specimens. The SAD patterns were used to determine the crystalline phases present in the specimen. The apertures used for the selected areas were 0.5 μ m in diameter, and thus for the highest resolution images presented the associated SAD patterns show the diffraction from a much larger area than shown in the image.

6.3 Results

6.3.1 α -phase

6.3.1.1 Image contrast in the α -phase

The results of an HREM examination of α -phase rare earth films are shown in Figure 6.1. Figure 6.1(a) shows an image of a single crystal thin film of Y and Figure 6.1(b) an image of a single crystal thin film of Ho, both imaged along the $[2\bar{1}10]$ direction in the rare earth. Simulations of the structure of Ho and Y are shown inset in the images, and there is a good qualitative match between simulation and image. The model used for the simulations was of the hexagonal close-packed structure of the heavy rare earths as discussed in section 2.2.1. As can be seen in the images of Figure 6.1, but more obviously in

the images of holmium/yttrium superlattices (for example Figure 6.4(a)), holmium appears darker than the yttrium. This effect arises from the incoherent elastic scattering of electrons. This scattering is highly dependent on both atomic number, Z , and thickness, and it is expected that for the same thickness of specimen, high Z regions will scatter more than low Z regions. Hence an image of a higher Z material will appear darker. Similarly a thicker region will scatter more electrons than a thinner region of similar Z . The images of the layers within the superlattice confirm that it is the difference in Z ($Z(Y)=39$, $Z(Ho)=67$) that is responsible for the different contrast observed for the two layers, as adjacent areas within a superlattice should be of similar thickness.

The observed images of Ho and Y are different from one another. In the image of the

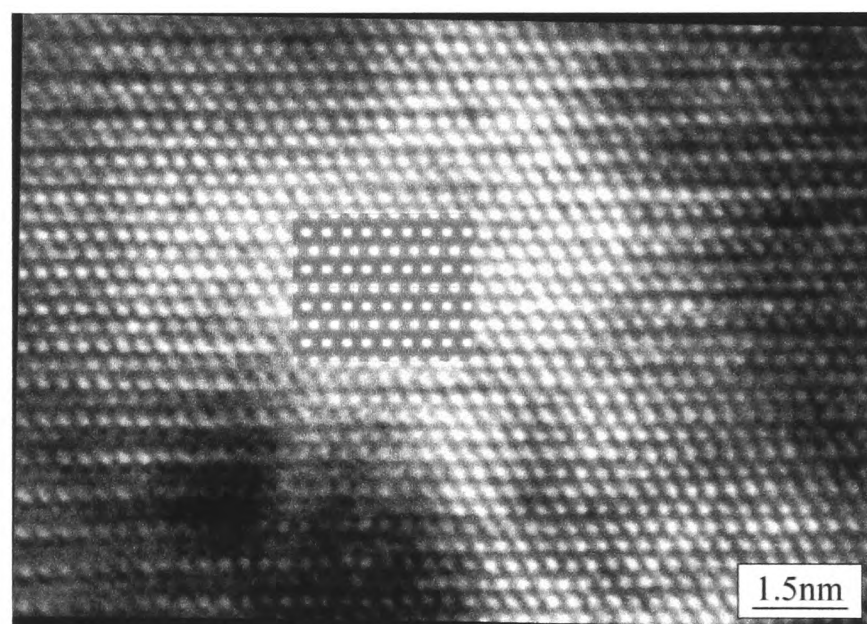


Figure 6.1 (a): yttrium metal, imaged along $[2\bar{1}10]$ with simulation inset

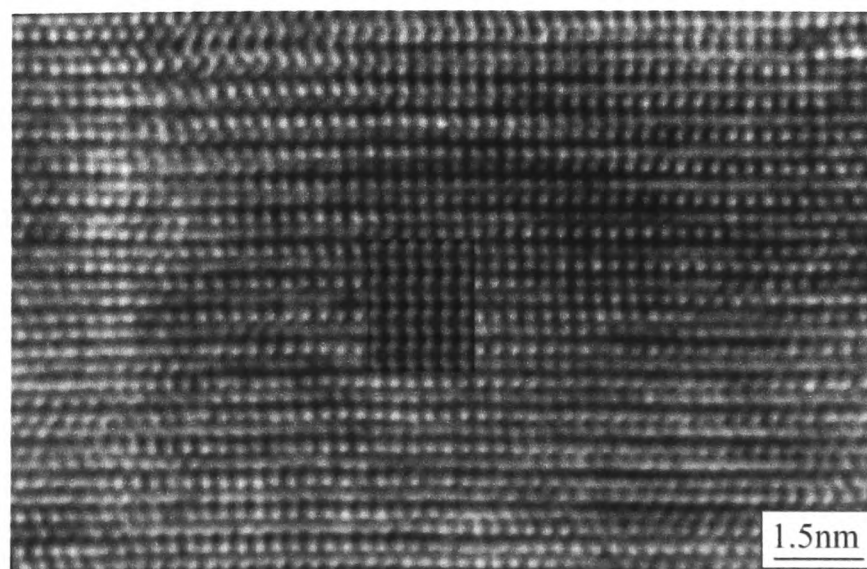


Figure 6.1 (b) : holmium metal, imaged along $[2\bar{1}10]$ with simulation inset.

yttrium film the $\{0002\}$ planes lying in the growth plane, $d_{0002}=0.2865\text{nm}$ and the $\{0\bar{1}11\}$ planes, $d_{0\bar{1}11}=0.2765\text{nm}$, lying at an angle of 61.4° to the growth plane are clearly visible. In the image of Ho the $\{0002\}$ planes lying in the growth plane, $d_{0002}=0.282\text{nm}$, are visible, but this time it is the planes at 90° to the growth plane, i.e. the $\{0\bar{1}10\}$ planes with a plane spacing of $d_{0\bar{1}10}=0.31\text{nm}$, that are visible in the image. The diffraction pattern from a typical area of α -phase yttrium is shown in Figure 6.2. Diffraction patterns from α -phase Ho are similar with different spot spacings reflecting the different lattice parameters. The pattern is typical of an hcp metal structure viewed along the $[2\bar{1}10]$ direction, confirming that the TEM specimens are representative of the bulk, and are still in the α -phase.

The reason that different image contrast can be observed in different specimen areas is because the image contrast is dependent on both specimen thickness and defocus. Figures 6.3(a) and 6.3(b) show the simulation of a series of HREM images of Ho and Y respectively with different thicknesses and defocus. The defocus series shows clearly that the images of holmium and yttrium are different even at the same defocus and thickness. These HREM images illustrate beautifully why image simulation is necessary as there is not always an intuitive correlation between image and structure and the contrast can vary dramatically with thickness and defocus.

6.3.1.2 Strain relief in α -phase

As discussed in section 3.3, knowledge of the strain relief mechanisms within epitaxial systems is crucial for understanding the physical properties of the system. Using the theory of Downes *et al.* [5] as explained in chapter 3, equation 3.31 gives the critical thickness as;

$$h_c = \frac{b}{4\pi(1+\nu)\epsilon} \ln \left| \frac{h_c}{b} + 1 \right|$$

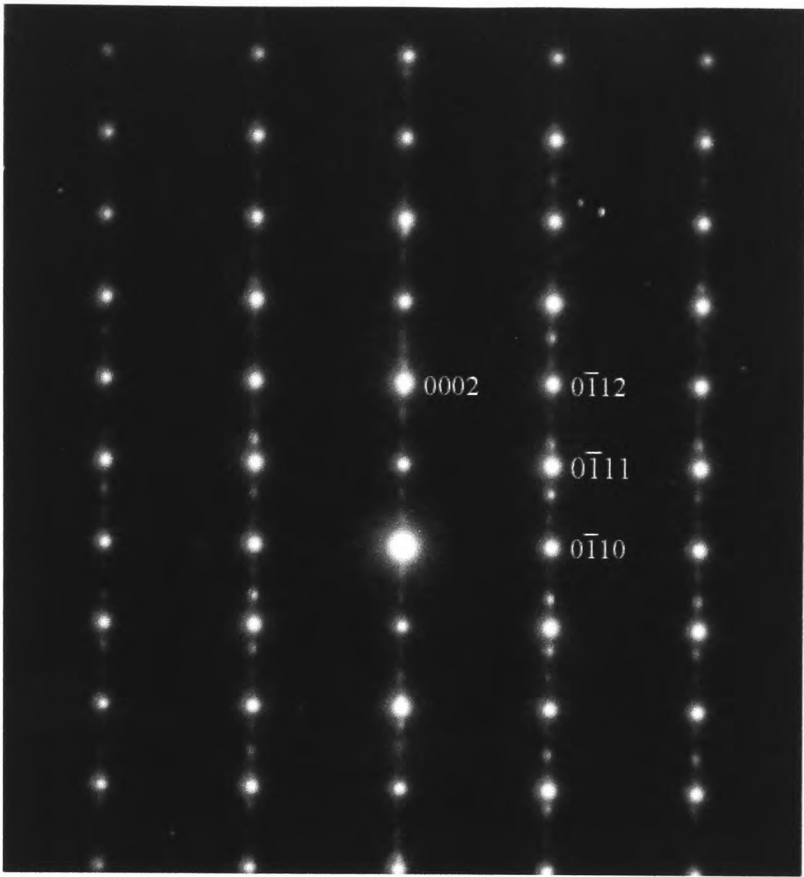


Figure 6.2: diffraction pattern of α -phase yttrium viewed along $[2\bar{1}10]$

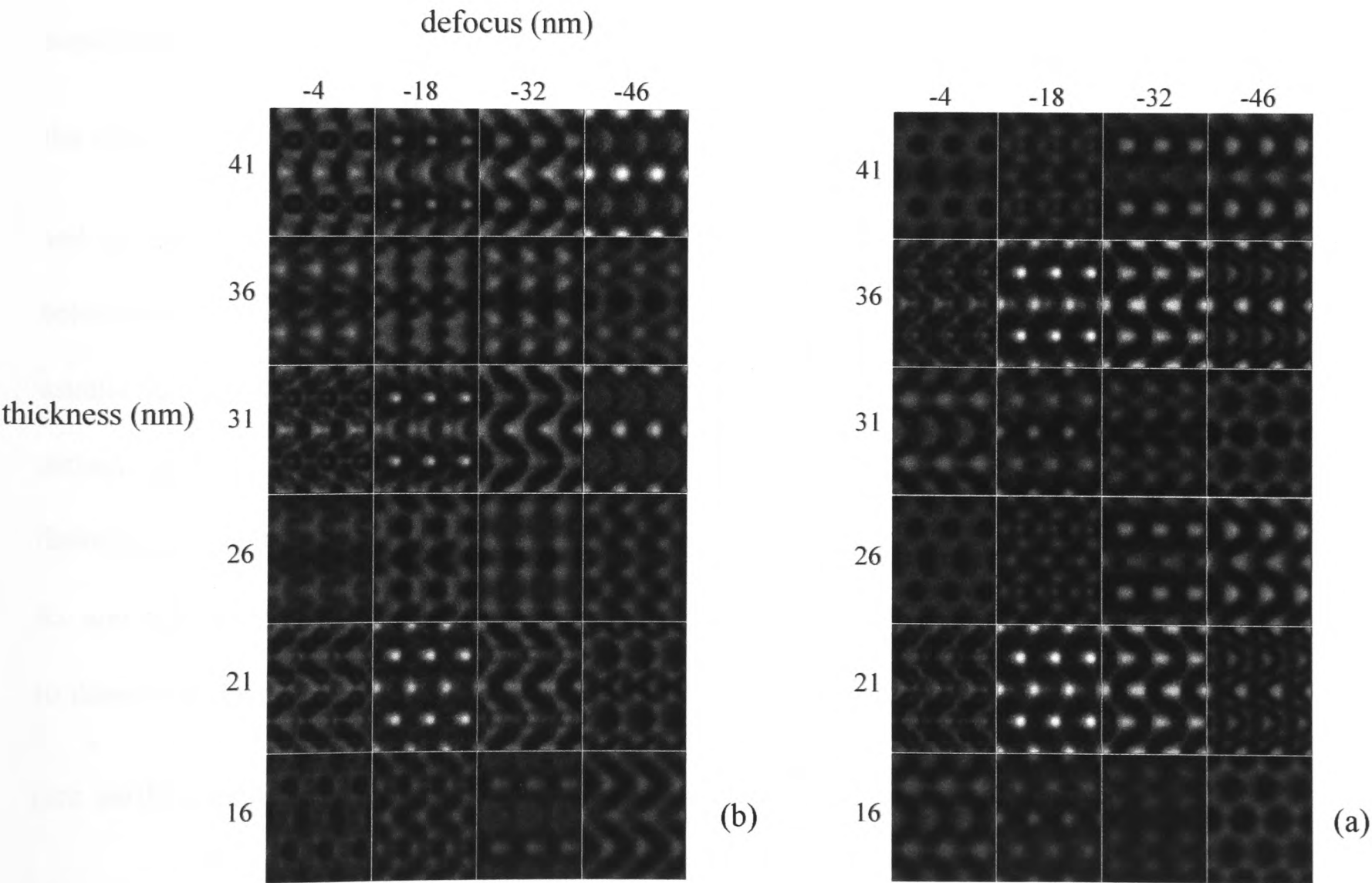


Figure 6.3: thickness/defocus image simulation of (a) holmium metal, (b) yttrium metal

For an yttrium layer on a holmium substrate, $\epsilon=0.01930$, $b=0.36471$ nm and $\nu\sim 0.5$. This gives a critical thickness of 4.3 nm, which is equivalent to approximately 15 monolayers. For a holmium layer on an yttrium substrate, $\epsilon=0.01967$, $b=0.3564$ nm and $\nu\sim 0.5$. The critical thickness of this layer is then 4.1 nm, or approximately 14.5 monolayers.

Figure 6.4(a) shows an image of a section of a Ho/Y α -phase superlattice (with the holmium layers dark and the yttrium layers bright) and 6.4(b) shows a higher magnification image of part of Figure 6.4(a) showing a misfit dislocation at the interface. The film was grown as 40 monolayers of holmium, 20 monolayers of yttrium repeated 30 times. Therefore both layers were above the calculated critical thickness implying that misfit dislocations could indeed be present.

Figure 6.5 (a) and (b) also show typical misfit dislocations as observed in a Ho/Y superlattice with both layers above the critical thickness. The Burgers vectors observed in the image are $\underline{b}=\frac{1}{3}[0\bar{1}10]$. In Figure 6.5(b) an extra plane is annihilated within the Ho layer and in Figure 6.5(a) an extra plane is inserted in the yttrium layer to relieve the strain between Ho and Y. The in-plane lattice parameter of Ho is 1.9% smaller than that of Y. It is usually the case that the Burgers vector of a crystal is the shortest lattice vector. However, in certain cases a dislocation can reduce its strain energy by dissociating into two partial dislocations. This is not generally observed, as often the fault has a high energy. However in fcc and hcp stacked systems the fault has a rather small energy, and so the dislocation is able to dissociate. From Figure 6.5 it can be concluded that for the α -phase hcp structure of the rare earth system the Burgers vector of the misfit dislocation is $\underline{b}=\frac{1}{3}\langle 11\bar{2}0 \rangle$ and the slip plane is the (0001) plane. The $\langle 11\bar{2}0 \rangle$ slip vectors are coplanar and form a network of dislocations in the basal plane. A dislocation can dissociate into two partials leaving a fault, which is essentially a small region of fcc stacking, lying between them.

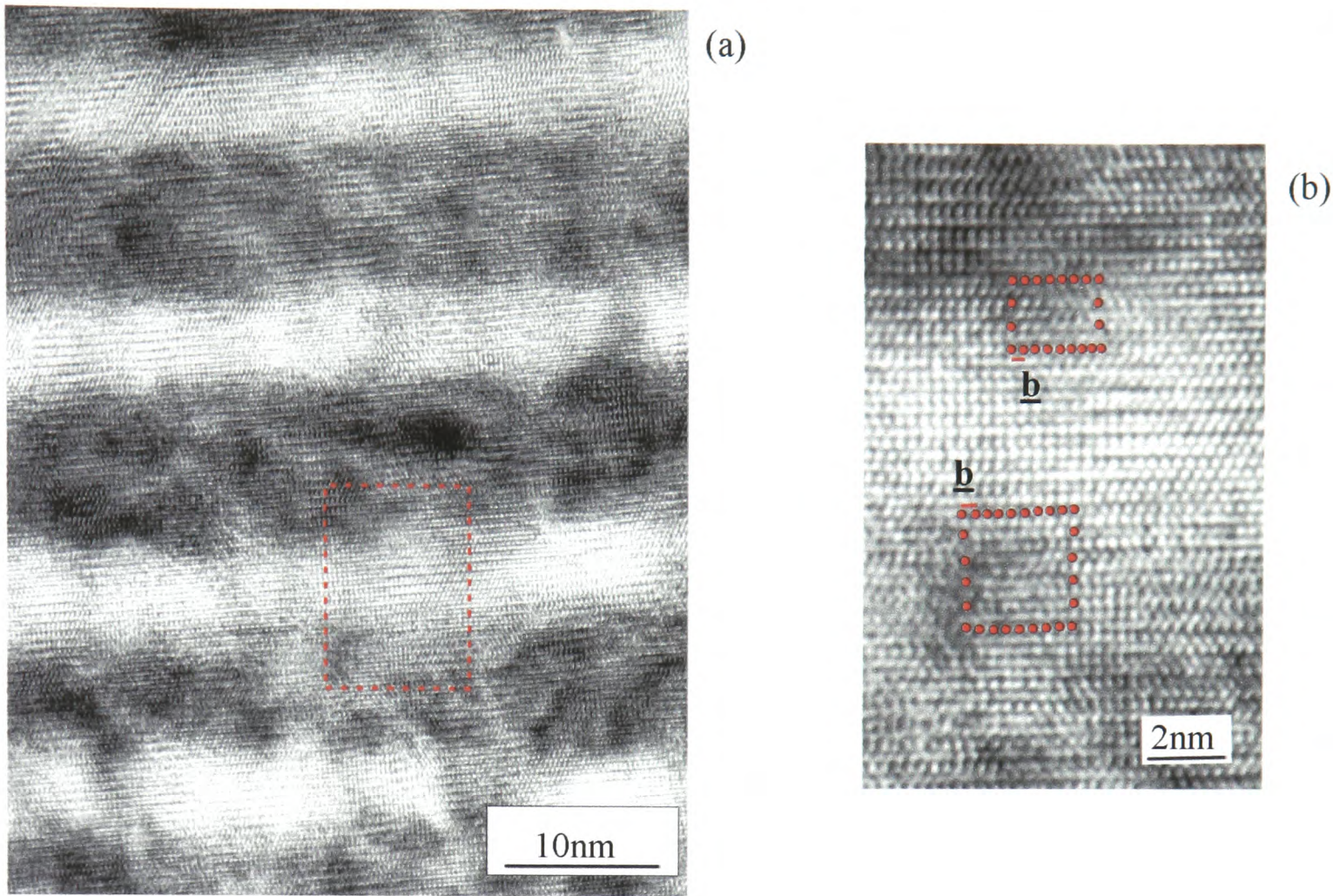


Figure 6.4 (a) Low magnification image of a Ho/Y superlattice showing the structure of 40 monolayers of Ho and 20 monolayers of Y, and (b) higher magnification image showing misfit dislocations

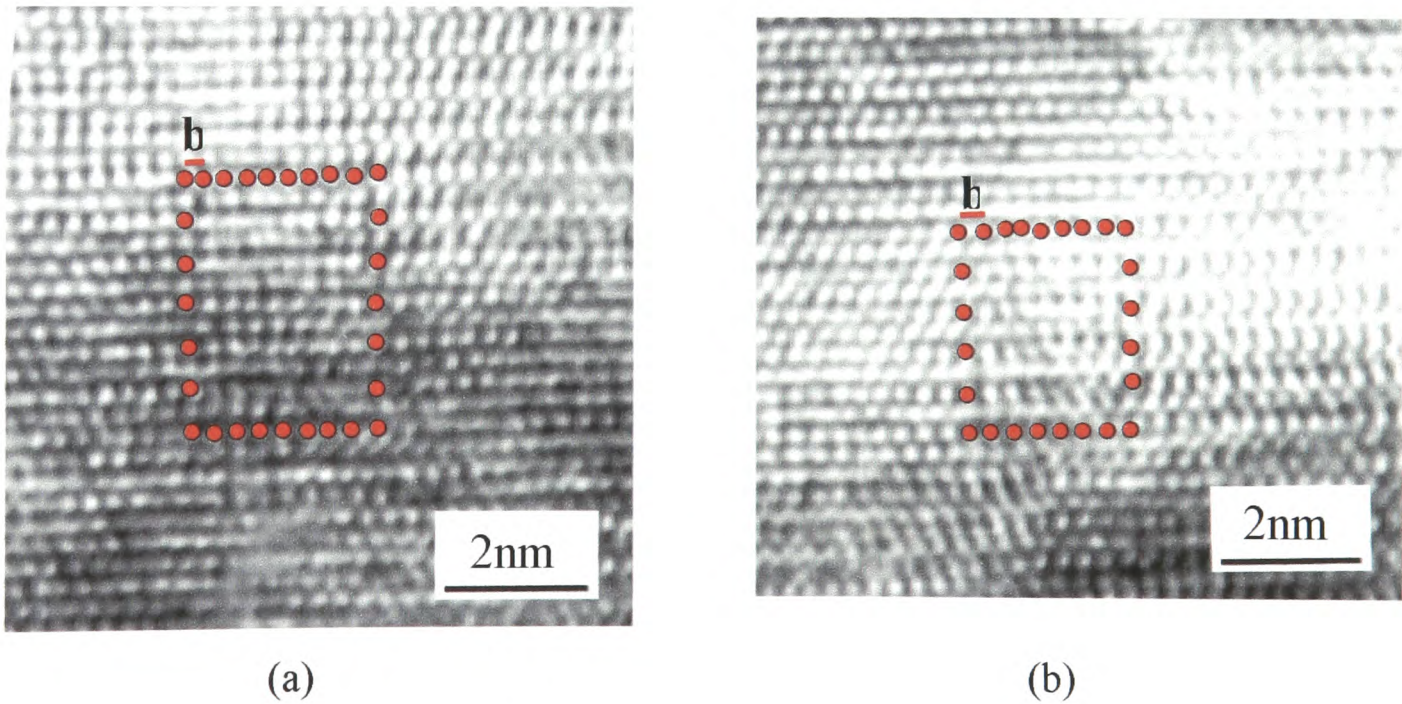


Figure 6.5: Typical images of misfit dislocations in a Ho/Y superlattice, with (a) showing a misfit dislocation at a Ho/Y interface, and (b) showing a misfit dislocation in an yttrium layer, showing that strain relief is not located entirely at the interface

The splitting of the dislocation can be written as;

$$AB \rightarrow A\sigma + \sigma B$$

$$\frac{1}{3}[\bar{1}2\bar{1}0] \rightarrow \frac{1}{3}[01\bar{1}0] + \frac{1}{3}[\bar{1}100]$$

and this is shown schematically in Figure 6.6.

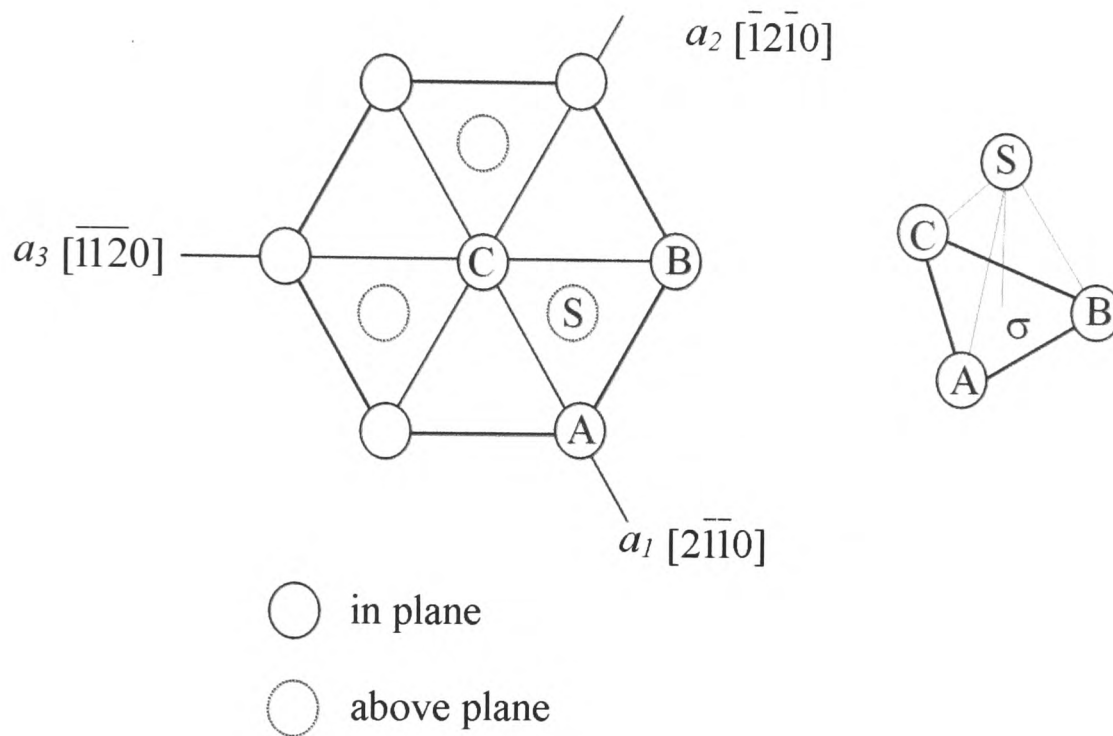


Figure 6.6: Atoms and lattice vectors in a hexagonal metal

From the theory of Dunstan *et al.* [6] which considers the relaxation of the strain above the critical thickness, as discussed in section 3.3.2.5, the strain present in the system for thicknesses just above the critical thickness will be of order $\sim 1.3\%$ and so the change in lattice parameters is not measurable by electron diffraction techniques, where the errors in the measurement are at best $\sim 2\%$. For full relaxation of the strain in the layers a misfit dislocation would be needed every 50 planes. This is not observed in Figure 6.4(a) and so, although not directly measurable, there is residual strain present within the system.

The effect of strain on the physical properties has been considered by different groups, for example the Oxford group have studied Ho/Y superlattices with XRD [7,8] and the group from Nancy have studied the magnetoelastic effects on Dy layers [9]. Both groups conclude that the systems are free from misfit dislocations, although they do not seem to have considered the possibility of the presence of both misfit dislocations and a residual strain present within the system due to incomplete relief of all the strain. The results of both groups are discussed in the light of the evidence from the HREM analysis that shows that misfit dislocations do exist within such systems.

The work on Ho/Y superlattices carried out by the Oxford group uses XRD analysis to extract quantitative data from longitudinal scans by fitting a model to the data. The model included the parameters N_A and N_B (the number of lattice planes per layer), ω_A and ω_B (the variances in N), d_A and d_B (the out-of-plane lattice parameters), the disorder parameter and the interdiffusion parameter, where the subscripts A and B refer to layers A and B respectively. They obtained an excellent fit to their data and from this fit they extracted among the other parameters the c-lattice constants of the two layers. They have not however published values for the in-plane lattice parameters, although scans along the $[10\bar{1}]$ direction reveal only one set of peaks and from this they have drawn the conclusion that the interfaces are coherent [private communication]. This is not necessarily the only conclusion that can be drawn from the observation of the aligned peaks. Kidd *et al.* [10] showed using x-ray reciprocal space mapping that for films above the critical thickness h_c , x-rays scatter coherently from the perfect epitaxial layer, and incoherently from the distorted regions around dislocations. Thus from just considering the coherent scattering from such structures the interfaces would appear to be completely coherent, though in fact they are semicoherent.

The effects of strain on a 60 nm epitaxial dysprosium film, grown between two thick erbium layers, have been reported by Dumesnil *et al.* [9]. They reported an increase in the

Curie temperature as the epitaxial strain increases (as measured from out-of-plane lattice parameters). They concluded from neutron diffraction patterns taken around a $(10\bar{1}0)$ reflection that the in-plane lattice parameters are the same because the width of the diffraction peak is smaller than the difference between the lattice parameters of bulk dysprosium and erbium. The change in Curie temperature indicates that there is strain present within the system, but it is possible that for a Dy film 60nm thick that there are misfit dislocations present with a proportion of residual strain remaining within the system. As the in-plane difference in lattice parameter between bulk Er and Dy is only $\sim 1\%$, if partial relaxation had occurred the separation of the $(10\bar{1}0)$ reflections for the Dy and Er would be smaller than the width of the diffraction peak, and so a scan around a $(10\bar{1}0)$ reflection would indeed reveal only one peak.

6.3.1.3 Specimen thickness limit

It has been mentioned that there is a limit on the thickness of a TEM specimen that it is possible to make of an α -phase metal, as thinner specimens take in hydrogen and form the dihydride. The thickness at which this occurs is different for Ho and Y, as can be seen in Figure 6.7 of a Ho/Y superlattice where the Ho layers are in the α -phase but the yttrium layers have changed to the β -phase. To estimate the limiting thickness of the specimens at which it is possible to prepare the α -phase, simulations were matched with both layers in a holmium/yttrium superlattice. As adjacent layers in a superlattice in the same micrograph should have similar thickness and defocus, by accurately matching simulations of the two structures into the layers (using simulations of the same thickness and defocus) it was possible to estimate the thickness of the specimen. Figure 6.8(a) shows an area of Figure 6.7 at higher magnification, and Figure 6.8(b) is an image from a different superlattice specimen with both holmium and yttrium in the α -phase. The inset simulations in Figure

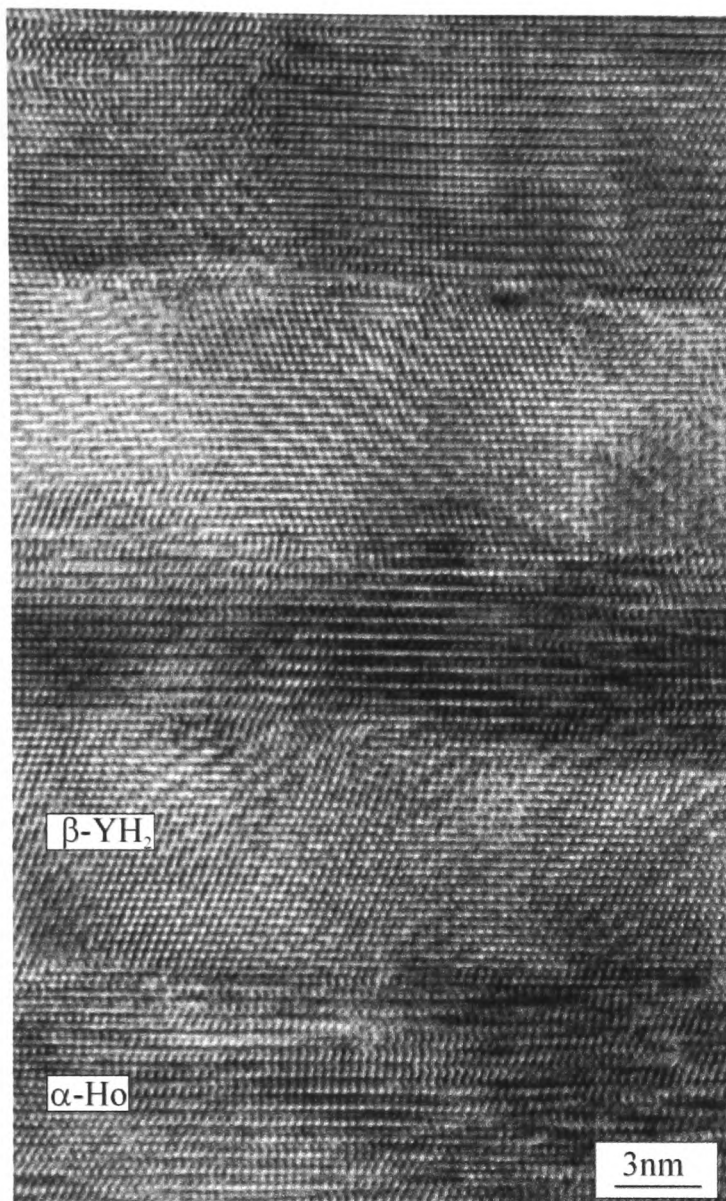


Figure 6.7: image of a Ho-Y superlattice where the holmium layers are still in the α -phase, but the yttrium layers have completely formed the β -phase dihydride

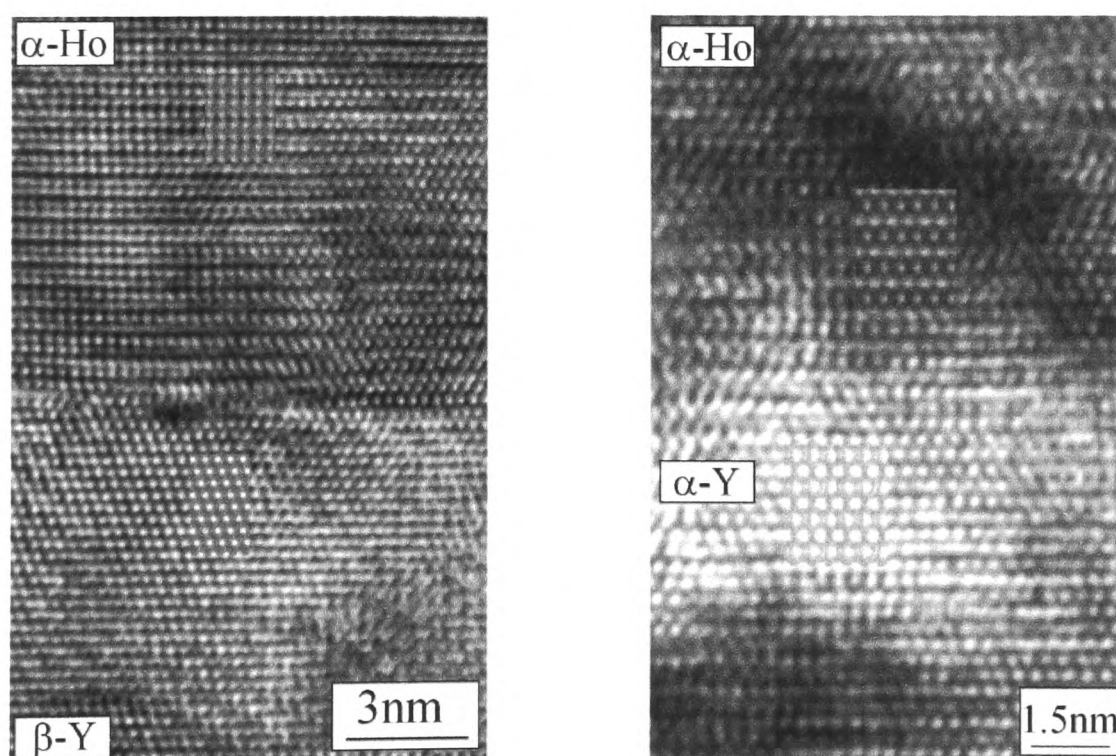


Figure 6.8: (a) image of a Ho/Y superlattice, viewed along $[2\bar{1}10]$ showing α -phase Ho and β -phase Y. Simulations of the structures are inset. From the simulation the thickness of this superlattice is 21nm. (b) image of a Ho/Y superlattice, viewed along $[2\bar{1}10]$. Both metals are in the α -phase, but the specimen is considerably thicker as seen by the reduced contrast in the image. The inset simulations suggest the specimen thickness to be 41nm.

6.8(a) were for specimens with thickness 21nm and defocus -46nm , and in Figure 6.8(b) the simulations were for specimens of thickness 41nm and defocus -46nm . In Figure 6.8(a) the α -phase Ho displays the same crossed $\{0002\}$ and $\{0\bar{1}10\}$ fringes as in Figure 6.1(b). The β -phase YH_2 layers show an image of a face-centred cubic structure viewed along $[\bar{1}10]$ with one set of $\{111\}$ planes, $d_{111}=0.301\text{nm}$, lying parallel to the growth plane, and another lying at 70.5° to the growth plane. In order to estimate the thickness below which the specimens are in the RH_2 phase a comparison with α -phase images of Figure 6.1 is made. Simulations of the image shown in Figure 6.1(a) suggest that the yttrium thickness is 26nm. Similarly simulations of the image shown in Figure 6.1(b) suggest that the holmium thickness is 21nm. Over a series of specimens α -phase yttrium (holmium) has not been observed for specimens of thickness less than 26 (21) nm. β -phase yttrium (holmium) hydride has been observed in specimens of thickness less than or equal to 21 (16) nm. This suggests that the thickness at which yttrium forms the dihydride is between 21–26nm, and for holmium the thickness is 16–21nm. Comparison of the enthalpies of formation of the β -phase dihydrides of holmium and yttrium show that they are very similar [11], and so it is not immediately obvious as to why all the yttrium forms the dihydride before any of the holmium undergoes the phase change.

6.3.2 β -phase

Figure 6.9(a) shows a characteristic image of HoH_2 and Figure 6.9(b) of YH_2 imaged along the $[\bar{1}10]$ direction. Figure 6.10 shows a $\beta\text{HoH}_2/\beta\text{YH}_2$ superlattice. The images are all taken from specimens that formed the hydride during specimen preparation, although comparison with images of specimens made from films that were loaded with

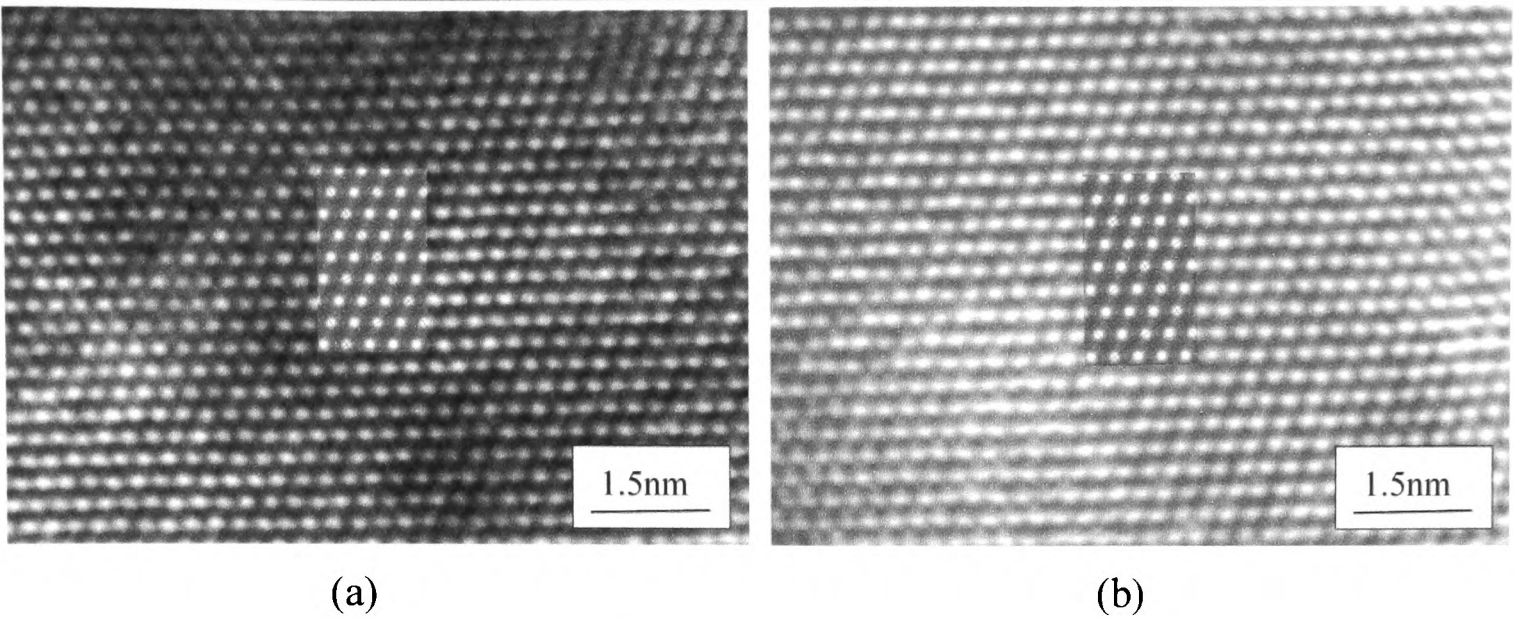


Figure 6.9: (a) HoH₂ imaged along $[110]$ with simulation inset (b) YH₂ imaged along $[110]$ with simulation inset

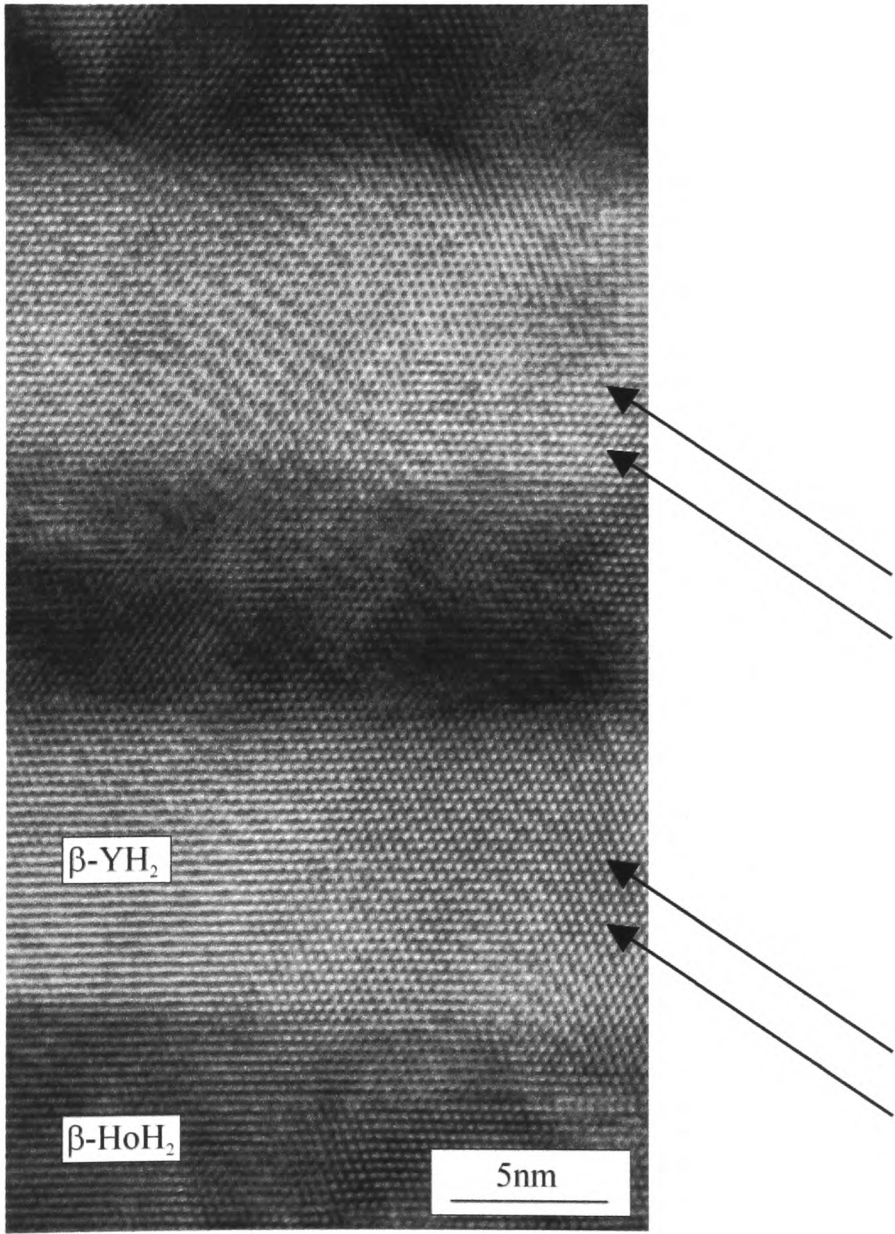


Figure 6.10: HoH₂/YH₂ β -phase superlattice imaged along $[110]$ the arrows indicate the Moiré fringes observed on many dihydride images

hydrogen ex-situ to the dihydride phase revealed no discernible difference. The lattice planes visible are the $\{111\}$ planes in the growth plane, with $d_{111}(\text{HoH}_2)=0.2982\text{nm}$ and $d_{111}(\text{YH}_2)=0.301\text{nm}$, and another set of $\{111\}$ planes at 70.5° to the growth plane. Both images have simulations inset. The diffraction pattern of an untwinned area of dihydride is shown in Figure 6.11.

As discussed in chapter 3, there is a unique orientation relationship for the rare earth metal/ niobium interface, but when the dihydride forms the symmetry of the structures about the growth direction reduces from 6-fold (α -phase) to 3-fold (β -phase) and thus there are two equivalent orientations that the β -structure can adopt. Figure 6.12 shows a typical twin boundary observed in HoH_2 . The twin boundary lies just in the basal plane. Figure 6.13 shows the diffraction pattern of an area of twinned dihydride.

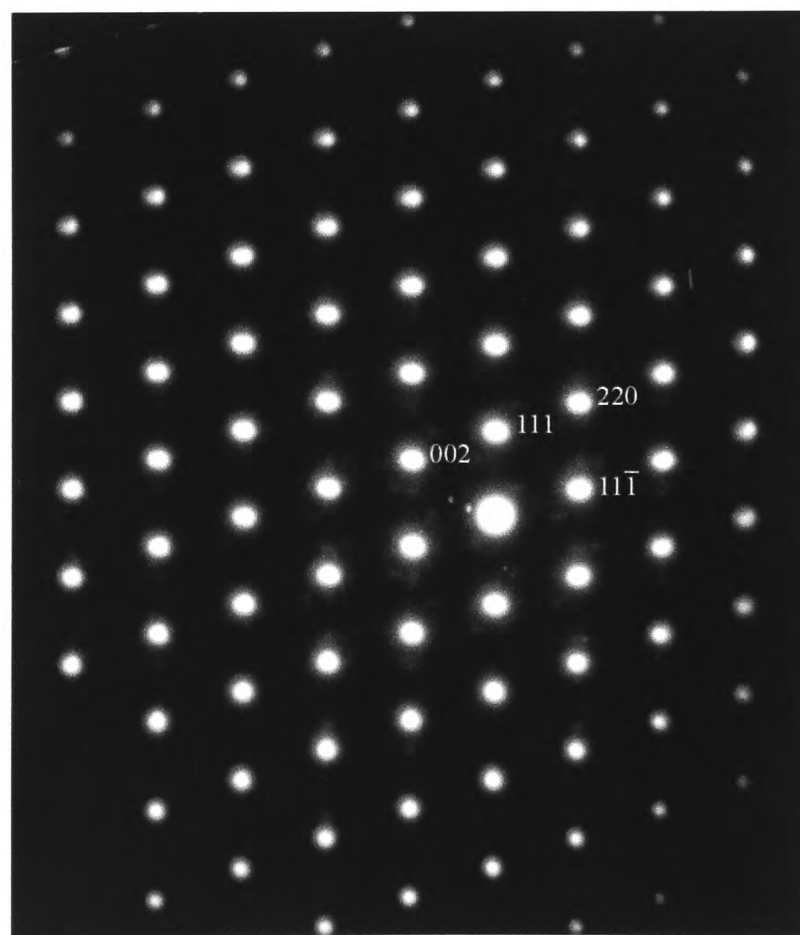


Figure 6.11: diffraction pattern along the $[\bar{1}10]$ beam direction for β -phase HoH_2

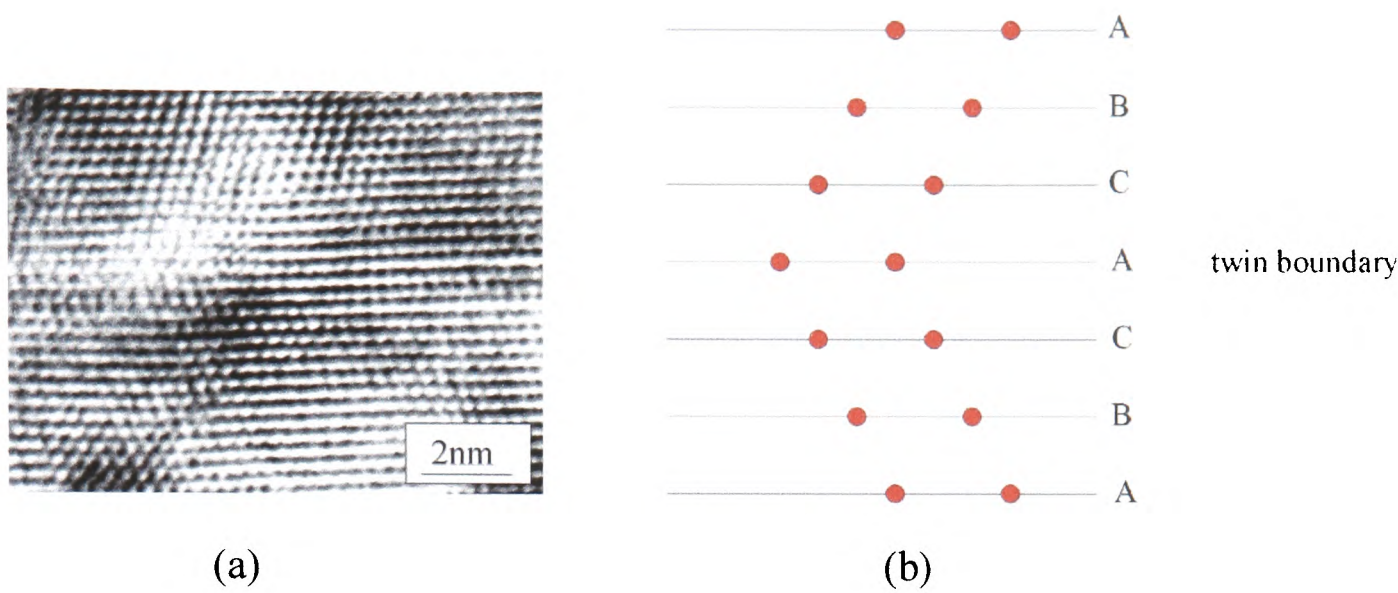


Figure 6.12: (a) image of YH₂ imaged along $[\bar{1}10]$ showing a twin boundary lying in the growth plane (b) schematic diagram of twin boundary

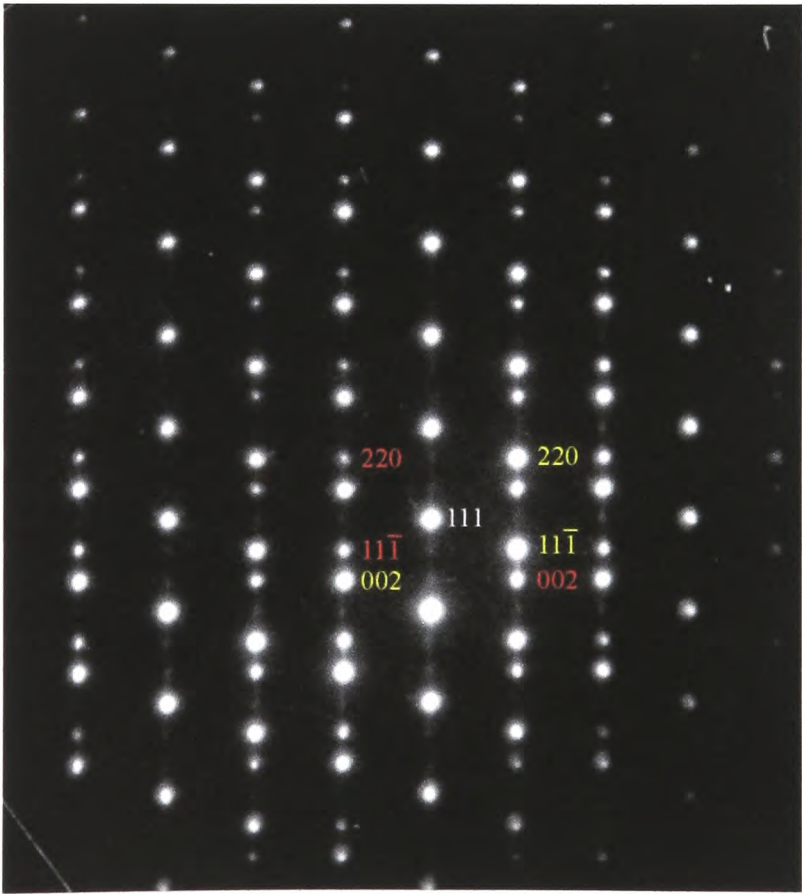


Figure 6.13: diffraction pattern along the $[\bar{1}10]$ beam direction for β -phase HoH₂, showing clearly that the structure is twinned. The (111) spot common to both patterns is labelled with white text, with the remaining diffraction spots labelled in red or yellow respectively, indicating the different twins

An important point to notice in the images of the dihydride are the faint Moiré fringes at an angle of $\sim 35^\circ$ to the growth plane. Moiré patterns form by the interference of two sets of lines with nearly common periodicities. The faint Moiré fringes observed on the dihydride images result from the presence of an epitaxial sesquioxide, R_2O_3 , on the specimen. The sesquioxide has also been observed from XRD measurements on films that have been hydrogenated *ex-situ* (shown in Figure 7.1). The formation of epitaxial R_2O_3 as a minor component of the hydrogenated films could be due to reaction with residual water vapour or (less likely) oxygen during loading or preparation, or by subsequent reaction in air. It is known that the ageing process of the heavy rare earth metals involves reaction with water vapour to form the dihydride [12] and then further reaction to eventually form the sesquioxide, which is thermodynamically by far the most stable compound (for example the free energy of Y_2O_3 is -1791 kJmol^{-1} whereas the free energy of YH_2 is only -181 kJmol^{-1}). The sesquioxide belongs to the space group $Ia\bar{3}$ (no. 206) and is body-centred cubic. The lattice parameters are 1.0602nm and 1.0607nm for Y_2O_3 and Ho_2O_3 respectively. The oxide structure is closely related to the hydride structure, with the oxide unit cell based on 8 unit cells of fluorite RO_2 with essentially $\frac{1}{4}$ of the oxygen atoms, those that lie along the $\langle 111 \rangle$ directions, in this network removed. Thus it is possible to consider a pseudo-fluorite R_2O_3 unit cell with a reduced a_0 of 0.503nm, although it must be remembered that the oxygen atoms in R_2O_3 break the fcc symmetry and thus the structures are different. From this pseudo-fluorite R_2O_3 unit cell it can be understood why there is a unique 3-dimensional orientation relationship between the oxide and the hydride, such that the orientation relation between the dihydride and the oxide is defined by the planes $\{111\}_{\text{fcc}} \parallel \{222\}_{\text{bcc}}$ and the direction $[\bar{1}10]_{\text{fcc}} \parallel [\bar{1}10]_{\text{bcc}}$ and imaging along the $[\bar{1}10]$ direction in the dihydride also images along a $\langle 110 \rangle$ type direction in the oxide. Figure 6.14 shows schematically how the

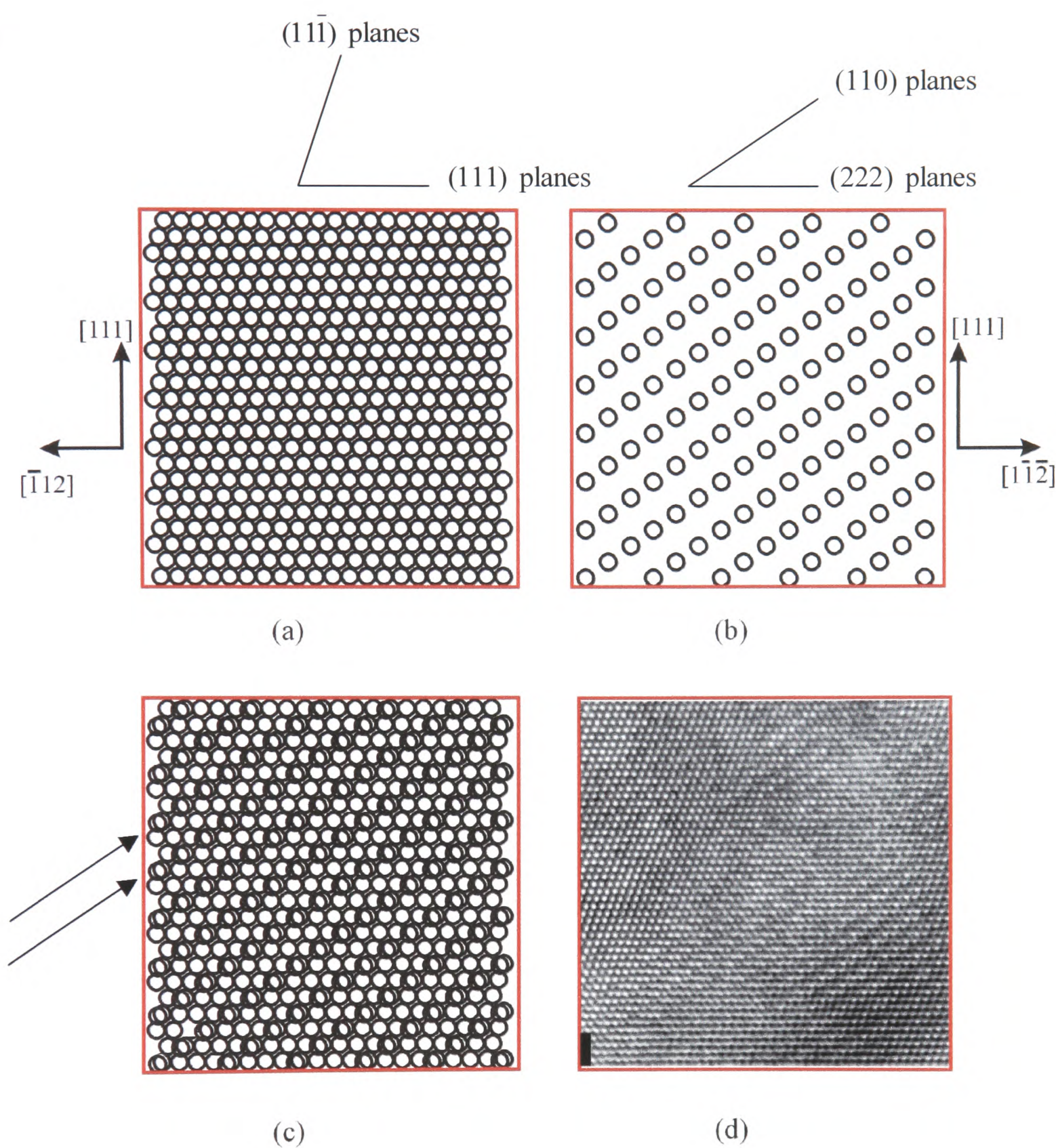


Figure 6.14: change in the image of rare earth dihydride, RH_{2+x} upon formation of a crystalline epitaxial oxide. (a)) schematic image along $[\bar{1}10]$ of fcc dihydride showing $\{111\}$ planes in the growth plane and at 70.5° to growth (b) schematic image along $[\bar{1}10]$ of bcc oxide, with $\{110\}$ planes lying at 35.3° to the growth plane(c) Moiré pattern simulation from combination of oxide and hydride (d) Image of HoH_2 along $[\bar{1}10]$ showing the Moiré pattern formed between oxide and hydride

presence of a thin layer of oxide on a TEM specimen surface would result in the formation of Moiré fringes. A schematic diagram of the image formed from the dihydride and from the oxide structure are shown in Figure 6.14 (a) and 6.14 (b) respectively. The interference between the two images would be seen as shown schematically in Figure 6.14 (c). The Moiré fringes are clear, lying at 35° to the growth plane. The schematic diagram and image agree qualitatively with the angle and the spacing of the Moiré fringes, and so confirm these fringes to be indicative of the presence of the oxide. The Moiré fringes in Figure 6.14 (d) are spaced $0.746 \pm 0.013 \text{ nm}$ apart (compared with a calculated spacing of 0.75 nm). Figure 6.15 shows the diffraction pattern of a twinned area of dihydride with a thin epitaxial oxide present on the specimen surface. The spots resulting from the oxide have been outlined in red in

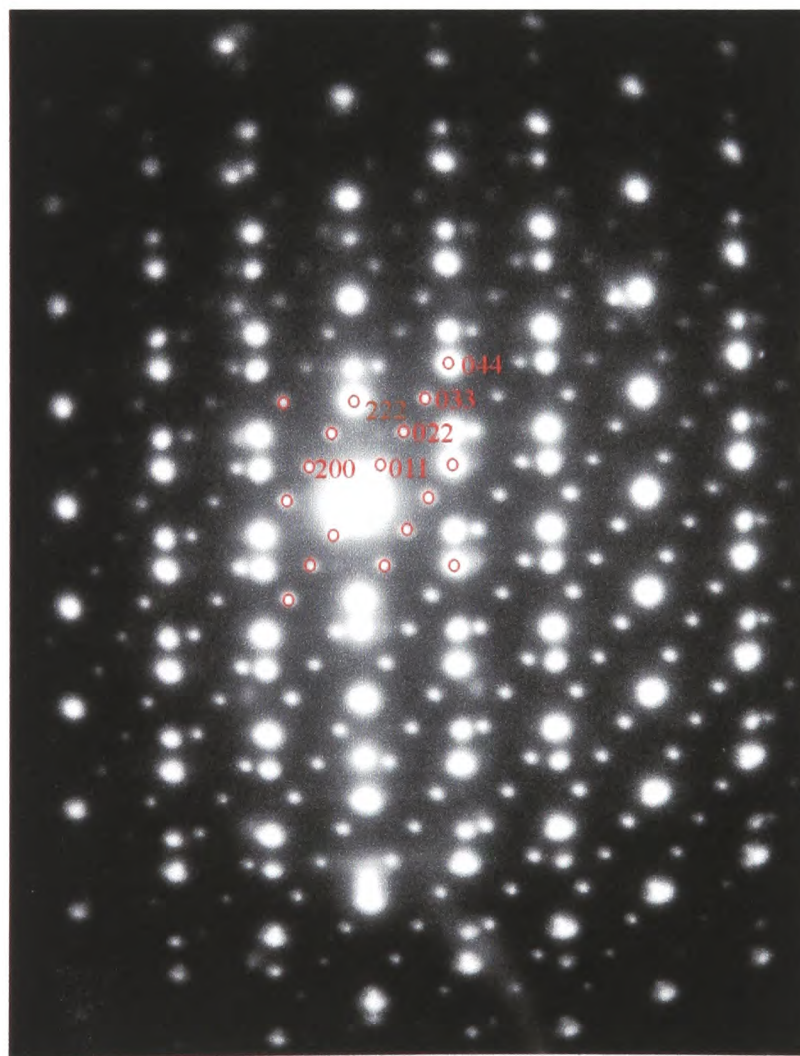


Figure 6.15: diffraction pattern along the $[\bar{1}10]$ beam direction for β -phase HoH_2 , showing clearly that the structure is twinned. The additional spots present in the pattern are from the epitaxial oxide R_2O_3 and have been outlined in red for clarity. Only the oxide spots are labelled, for the dihydride labelling refer to Figure 6.14

red for clarity, and are clearly less intense than the spots due to the hydride, indicating that the oxide is a minor component of the specimen. For full indexing of the pattern shown in Figure 6.15, the hydride pattern can be indexed with reference to Figure 6.13.

6.3.3 γ -phase

It has not been possible to prepare specimens from γ -phase bulk films as the trihydride film unloads hydrogen under uncapped vacuum conditions. It is thus expected that all uncapped thin film specimens would reach equilibrium very quickly with their surrounding atmosphere, resulting in the formation of the β -phase.

An image of a film of holmium trihydride (γ -phase), as identified by XRD before specimen preparation, is shown in Figure 6.16. Although the holmium dihydride structure

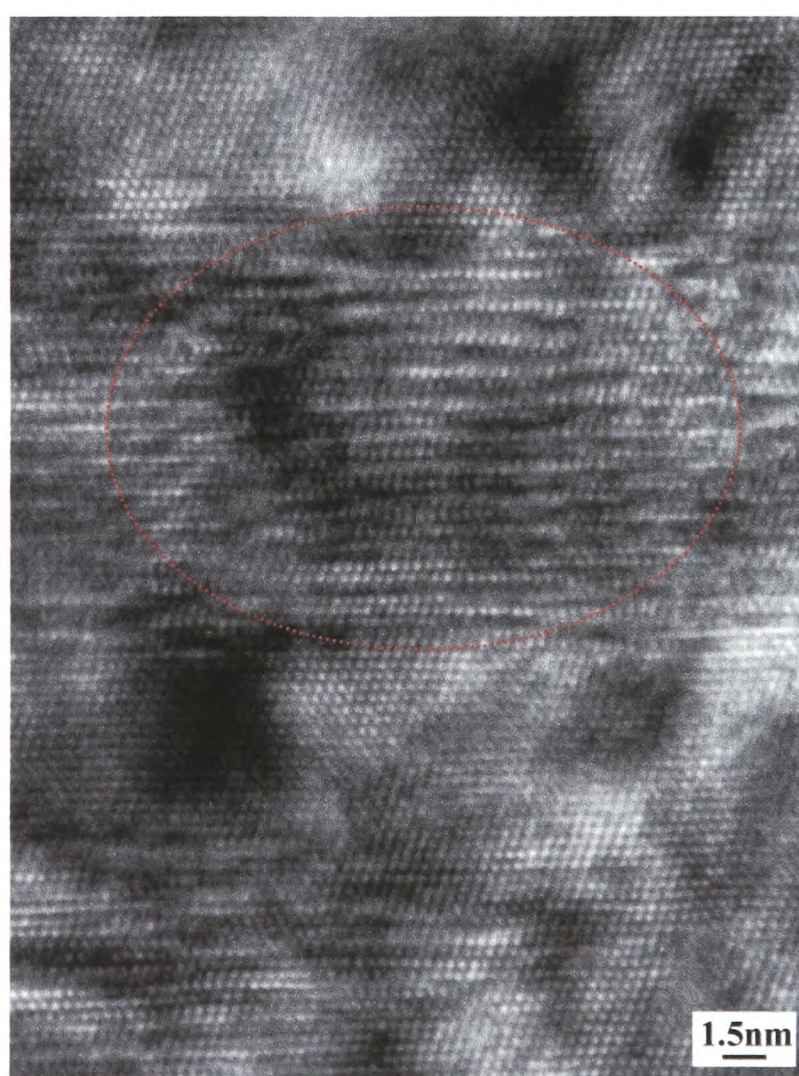
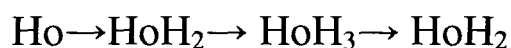


Figure 6.16: image of film that was HoH_3 (γ -phase) before specimen preparation. The specimen is predominantly β -phase, but large areas (indicated by red oval) show evidence that the crystal has had a different history to pure β -phase specimens

can be clearly seen in parts of the image, there are larger areas where the quality of the crystal has clearly been affected by the cycling of hydrogen. At this stage the specimen has the history



and is clearly different from the specimens that have only undergone the $\text{R} \rightarrow \text{RH}_2$ transformation. The contrast seen in this image is indeed characteristic of a specimen that has been loaded with hydrogen above stoichiometric $\text{RH}_{2.0}$ and the reason for such contrast is discussed in the next chapter.

6.4 Conclusions

The work reported in this chapter has shown that it is possible to prepare TEM specimens from rare earth thin films by employing the appropriate specimen preparation techniques. Conventional specimen preparation techniques, including broad ion beam milling, were found to produce specimens that were significantly changed from the initial film. The highly reactive nature of the rare earths led to various reactions occurring during specimen preparation and to the formation of the dihydride and oxide, frequently leaving no trace of the initial α -phase metal film. It is surprising, therefore, that Petford-Long *et al.* [1] have found it possible to prepare Gd by conventional methods where it has not proved possible to prepare Ho or Y specimens. Comparison of the enthalpies of formation of the β -phase dihydrides of these three elements are very similar [11] so the difference either lies with the W layers that somehow act to stabilise the Gd, or in the specimen preparation techniques employed, for which grinding, polishing and milling stages are all much longer for films grown on sapphire rather than for films grown on silicon substrates. For the rare earth thin films grown on a niobium/sapphire substrate system, α -phase specimens were prepared with a focused ion beam system. The success of this method over conventional

specimen preparation techniques was possibly a result of the shorter preparation time (of order 20 times less) or was due to the fact that specimens do not need to be cooled to liquid nitrogen temperatures within the focused ion beam system, and thus any problems of water condensation on the specimens and the associated reaction with water at the specimen surface during milling are avoided. Even with this preparation technique it was found that there was a limiting thickness above which it was possible to prepare α -phase specimens, and that for thinner specimens the dihydride had formed throughout the specimen thickness leaving no trace of the metal.

Analysis of the strain relief mechanisms present within the superlattices revealed the Burgers vector as $\underline{b} = \frac{1}{3} \langle 11\bar{2}0 \rangle$. Further work into the strain present within the system was excluded due to the small residual strains present ($\sim 1\%$) and the accuracy of d -spacing measurements with electron microscopy ($\sim 2\%$) in addition to the fact that in general TEM specimens do not have parallel sides, but are wedge shaped. This means that across the superlattice there are a range of thicknesses, and in many specimens this was observed to be true with thin areas exhibiting α -Ho - β -YH₂ layers, intermediate areas showing resolvable crossed lattice planes with both layers being in the α -phase and often much thicker areas showing unresolvable lattice planes. The effect of specimen thickness on the crystalline phase meant that the specimens were not wholly representative of the bulk film and so the strain relaxation must have been affected by the α - β phase transformation.

The work on the various crystallographic phases within the R-H system has confirmed the crystallographic structure and orientation of the various phases. It has also shown that there does appear to be degradation of the crystal quality during hydrogen cycling, as shown in the specimen prepared from a γ -phase thin film. The image shows regions of the specimen clearly in the β -phase but with large areas where the fringes are

indistinct. There is however a characteristic contrast associated with these layers, discussed more fully in the next chapter, and this is shown to be related to loss of structural coherence during hydrogen cycling. The presence of Moiré fringes on the images of the dihydride led to the discovery that an epitaxial oxide formed on the specimen surface. The presence of an oxide of the form R_2O_3 as a minor component of the hydrogenated specimens was also confirmed by XRD.

References

- [1] A. K. Petford-Long, P. E. Donovan, and A. Heys, *Ultramicroscopy* **47**, 323 (1992).
- [2] J. C. Bravman and R. Sinclair, *J. Electron Microsc. Tech.* **1**, 53 (1984).
- [3] K. Cherifi, P. E. Donovan, C. Dufour, P. Mangin, and G. Marchal, *Phys. Stat. Sol. (a)* **122**, 311 (1990).
- [4] M. Gasgnier "The intricate world of rare earth thin films: Metals, Alloys, Intermetallics, Chemical compounds,...", in *Handbook on the Physics and Chemistry of Rare Earths, Vol. 20*, edited by K. A. Gschneidner and L. Eyring, Elsevier Science,, 105 (1995).
- [5] J. R. Downes, D. J. Dunstan, and D. A. Faux, *Phil. Mag. lett.* **76**, 77 (1997).
- [6] D. J. Dunstan, S. Young, and R. H. Dixon, *Appl. Phys.* **70**, 3038 (1991).
- [7] D. Jehan, D. F. McMorrow, R. A. Cowley, R. C. C. Ward, M. R. Wells, N. Hagmann, and K. N. Clausen, *Phys. Rev. B* **48**, 5594 (1993).
- [8] D. F. McMorrow, P. P. Swaddling, R. A. Cowley, R. C. C. Ward, and M. R. Wells, *J. Phys. C* **6**, 6553 (1996).
- [9] K. Dumesnil, C. Dufour, P. Mangin, G. Marchal, and M. Hennion, *Europhys. Lett.* **31**, 43 (1995).

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- [10] P. Kidd, P. F. Fewster, N. L. Andrew, and D. J. Dunstan, in *Critical thickness phenomena: the distinction between the existence of interfacial dislocations and significant lattice relaxation*, Oxford, 1993 (Institute of Physics), p. 585.
- [11] P. Vajda "Hydrogen in rare-earth metals, including RH_{2+x} phases", in *Handbook on the physics and chemistry of rare earths, Vol. 20*, edited by K. A. Gschneidner Jr. and L. Eyring, Elsevier Science,, 208 (1995).
- [12] H. K. Smith, A. G. Moldovan, R. S. Craig, W. E. Wallace, and S. G. Sankar, *J. Solid State Chem.* **32**, 239 (1980).

Chapter 7

Hydrogen induced deformation of epitaxial (0001) holmium films

This chapter presents the results of investigations into the effect of loading epitaxial single crystal Ho films grown by molecular beam epitaxy on (110) Nb|| (11 $\bar{2}$ 0) Al₂O₃ substrates. Section 7.1 is an introduction to the system and an explanation of why it is of interest. The results from experiments made with XRD, AFM, UFM, SEM and TEM on three films of HoH_y, where nominally y=0,2,3 are presented in section 7.3. Section 7.4 is a discussion of the results for this system in the context of results from related systems.

7.1 Introduction

There is considerable interest in the hydrogen loading of rare earth elements, including holmium, because of their ability to absorb up to 3 hydrogen atoms per metal atom, which leads to a range of interesting properties. A comprehensive review of the properties and behaviour of bulk R-H systems has been given by Vajda [1]. The β -phase dihydride exists over a considerable range of hydrogen concentration. In the range RH_{2+x} the excess H atoms are effectively in solution in the octahedral interstitial sites of the fcc dihydride lattice and are free to interact with each other and form a hydrogen sublattice [2]. This ordering is observed as an anomaly in several physical properties [3,4] including the

magnetic properties. Another exciting feature is that during hydrogen loading there is a continuous decrease in the carrier density, which gives rise to a metal-insulator transition in the interval between RH_2 and RH_3 . It has been observed that metallic 'mirror-like' films become transparent upon hydrogen loading [5]. The loading is reversible and the switching time between mirror and transparent film is of the order of a fraction of a second for polycrystalline samples [6]. The systems are of interest both for the practical applications of switchable mirrors, and because of the possibility of real-time visualisation of hydrogen migration in metals [7]. Hydrogen in metals has been extensively studied as many metals can absorb hydrogen, and the hydrogen then drastically alters the mechanical, structural, electrical, optical, and magnetic properties of the systems. Due to the small mass of a hydrogen atom the diffusion is very fast, and so real time observation of such diffusion coupled with studies of the effect that the hydrogen has on the system is of great interest.

Studies of the hydrogen loading and switching of *epitaxial* films of (0001) Y on (110) Nb or (110) W have been reported by Wildes *et al.* [8], Remhof *et al.* [9] and Hayoz *et al.* [10], and of (0001) Y on (111) CaF_2 by Nagengast *et al.* [11] and Kerssemakers *et al.* [12]. These studies have shown that the single crystal nature of the films is preserved throughout the cycling between the α , β and γ phases, accommodating the changes of structure of the rare earth metal lattice (hcp (α) - fcc (β) - hcp (γ)). There are conflicting reports, however, about the extent of the deterioration in crystalline perfection which occurs as a result of loading/unloading cycles. The aim of the present work is to study in more detail the structural changes which occur during hydrogen loading of thin epitaxial films of holmium. Ho was chosen because of an allied interest in the effect of hydrogenation on the magnetic properties of the rare earths. The HoH_y films have been studied using X-ray diffraction, high resolution electron microscopy, secondary electron microscopy and the scanning probe techniques atomic force microscopy, AFM, and ultrasonic force microscopy,

UFM. In particular cross-sectional samples of these systems have been loaded with hydrogen in a controlled environment transmission electron microscopy, CETEM, for the first time.

7.2 Experimental Techniques

7.2.1 Sample growth

Three identical samples were studied consisting of a trilayer of 10nm Nb/ 300nm Ho/ 10nm Nb (the Nb capping layer was grown after cooling to room temperature because at elevated temperatures Nb grows in a 3D mode on rare earths, whereas at room temperature a more continuous layer is formed which consists of grains of twinned orientation). The films were sent to KTH, Stockholm, for hydrogen loading. One film was loaded to the trihydride phase, and one to the dihydride phase by heating in a UHV-based H reactor. The third sample was left in the as-grown state.

CETEM was used to study the in-situ hydrogen loading of the β -phase sample. Cross-sectional samples were prepared from all three samples by the methods detailed in section 4.3. The CETEM studies were performed using a side entry JEOL 4000EX operating at 400 keV, with a point-to-point resolution of 0.26nm. After examination in the as-prepared condition the sample was exposed *in-situ* to a hydrogen pressure of 20 mbar at a temperature of 220°C for 5 hours, and then the temperature was reduced to room temperature over 5 hours.

The samples were studied *ex-situ* using x-ray diffraction and optical transmission measurements. The x-ray work used a 2-circle diffractometer with a graphite monochromator in front of the detector and Cu K α radiation. The optical transmission

experiments were performed on all three samples at normal incidence using the 532nm second harmonic of a Nd-YAG laser and a Melles Griot laser power meter (relative precision approximately 0.1%). The nanoscale surface structure of the film was characterised using various microscopy methods. Secondary electron (SE) images were taken on a Hitachi S520 scanning electron microscope operating at 20 keV and a tilt angle of 40°. Atomic force microscopy was also used for surface topography imaging and ultrasonic force microscopy [13] was employed to detect any material differences in the surface layer. The scanning probe microscopy was carried out using a PARK-CP multiprobe instrument.

7.3 Results

7.3.1 XRD examination

Symmetric scans, i.e. measuring reflections from Bragg planes parallel to the surface, were performed by x-ray diffraction and the results are shown in Figure 7.1. Together with the RHEED measurements during growth of the samples, the XRD analysis confirms the single crystal nature of the layers before and after loading, with epitaxial relationships as described in section 3.2 and shown in appendix 1.

A single Bragg peak corresponding to the β -phase (111) lattice planes was observed in the XRD scan of the dihydride sample (Figure 7.1(b)). The lattice parameter of the dihydride in this sample was determined to be $a_{fcc}=0.513\text{nm}$ compared with the bulk value of 0.517nm. The dihydride lattice, HoH_{2+x} , contracts with increasing x , as shown in Figure 7.2, which is a result of the strong ionic character of the interaction of the lattice with the excess H atoms on the octahedral (o) sites [1]. It is concluded that the dihydride sample is single-phase and in the superstoichiometric range. It should also be noted, from the shift of

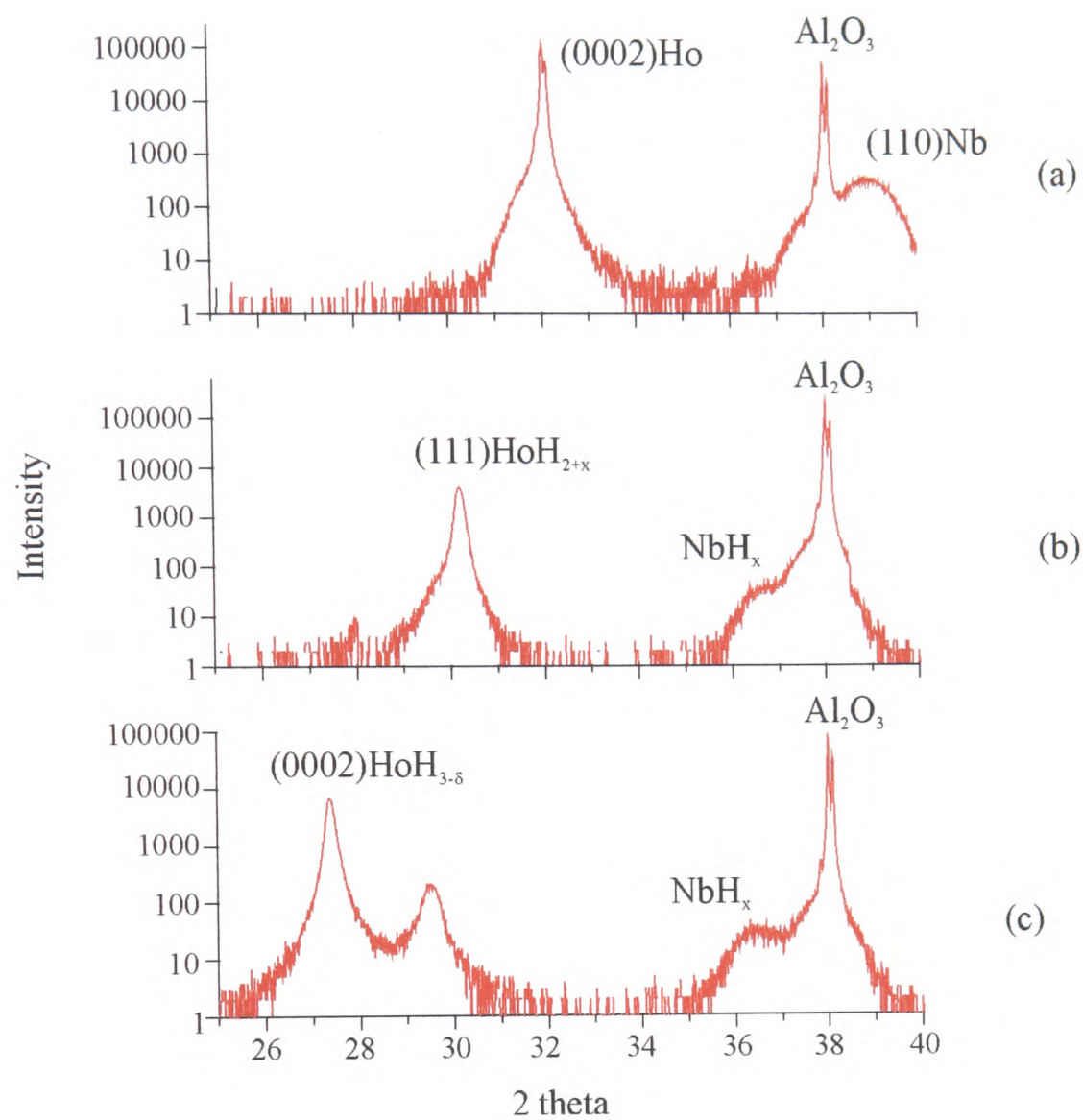


Figure 7.1: XRD spectra of (a) the as-grown metal, (b) the dihydride and (c) the trihydride sample

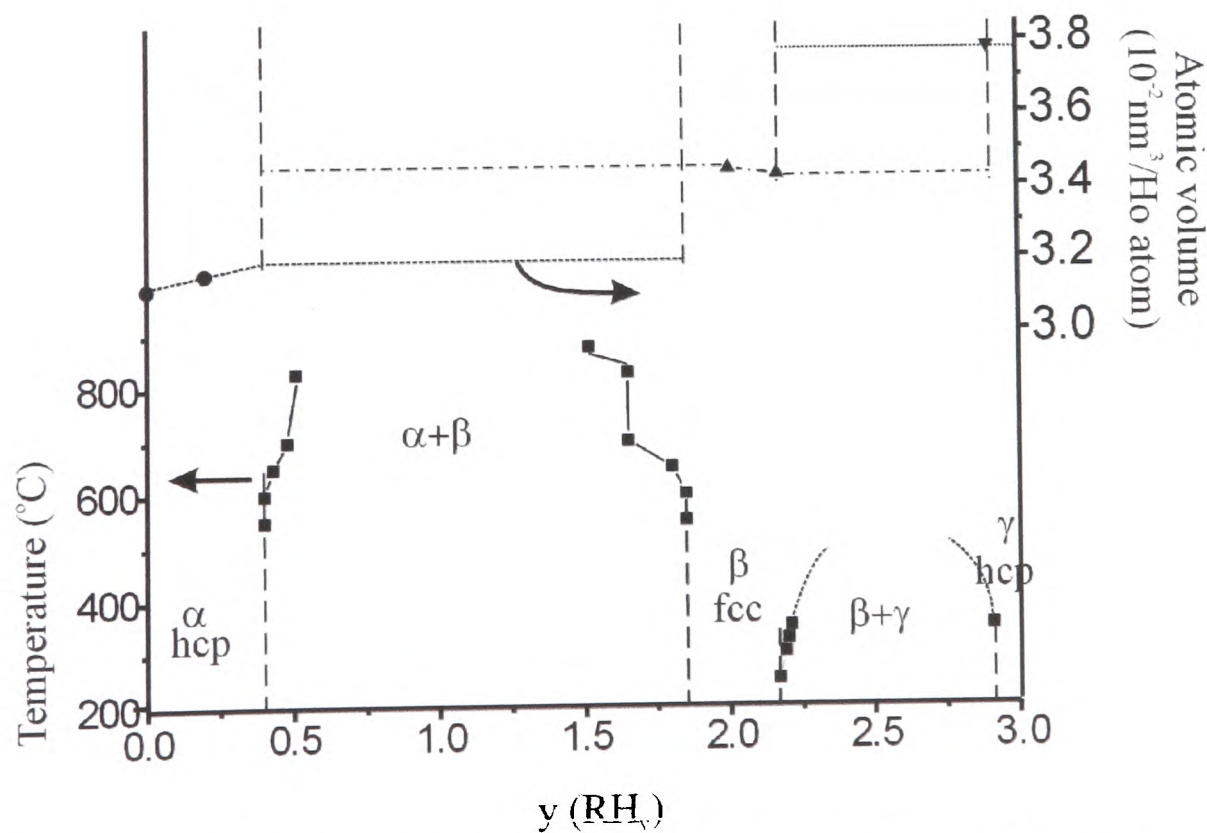


Figure 7.2: HoH phase diagram and the associated change in atomic volume V/R (where V is the volume of the unit cell, R is the number of Ho atoms per unit cell) with hydrogen concentration

the Nb (110) reflection to lower 2-theta, that the niobium layers have absorbed H during the loading process [14].

The trihydride sample, 7.1(c), exhibited a strong XRD peak corresponding to the HoH_{3-6} trihydride phase with c-axis lattice parameter $c_{\text{hcp}}=0.657\text{nm}$ (bulk value $c_{\text{hcp}}=0.656\text{nm}$). In addition a second, much weaker reflection is recorded at $2\theta \approx 29.5^\circ$ which is indexed as Ho_2O_3 (222) with lattice parameter $a_{\text{bcc}}=1.059\text{nm}$ (bulk value 1.061nm). The possibility that this peak could be attributed to residual dihydride which is strained by the surrounding trihydride matrix was also considered, but the necessary degree of strain is unreasonably large (cf. dihydride peak position in Figure 7.1(b)) and the identification as epitaxial oxide is thought more likely. Subsequent re-examination of this sample has revealed no change of this XRD pattern with time. Lastly, a slight further shift of the Nb-H peak is noted in the higher-loaded sample.

7.3.2 Optical Measurements

The optical transmission of the trihydride sample was found to be approximately 6%, compared to a value of only 0.0035% for the dihydride sample. The metal sample had an optical transmission of less than 0.0001% (the limit of our measurement setup). The ratio of optical densities of the HoH_2 and HoH_3 films (presuming the influence of the much thinner Nb layers is negligible) is then 5.8×10^{-4} . The change in the optical transmission from the reflective, shiny mirror of the metal to highly transparent in the trihydride phase, after accounting for the effect of the niobium buffer and cap layers, is confirmation that the film has undergone a metal-insulator transition.

7.3.3 Scanning Probe Microscopy

The AFM results (Figure 7.3(a)) show that there is a fine structure (appearing with lighter contrast) on the surface of the as-grown metal sample of scale 200-300nm and height

10-25nm, which was identified as grains of Nb. Thermodynamically it is not possible to achieve 2-D growth of niobium on rare earth underlayers as the surface free energy of niobium at 2.98 Jm^{-2} is significantly larger than that of yttrium (unfortunately there are no data available for holmium but presumably the heavy rare earths will be similar) where $\gamma=1.16 \text{ Jm}^{-2}$ [15]. Thus the inequality (3.1)

$$\gamma_f + \gamma_i - \gamma_s < 0$$

is not satisfied and so growth is 3-D. This is confirmed by RHEED measurements during growth which show that the Nb capping layer grows in a 3-D (island) mode with twinned orientations. This fine structure is clearly visible on both the dihydride and the trihydride samples, but there are additional linear, triangular features of order 300 nm wide, and 20-30 nm high. The AFM images in Figure 7.3 clearly show the emergence of the triangular features as ridges on the dihydride film surface, with a greater density of such features on the trihydride film. The linear features appear over the whole of the top surface, and are related to the crystallography of the layers. As the ridges are first seen in the dihydride sample, it is the crystallography of this fcc layer that will be used to define their orientation. The ridges are aligned with the $[0\bar{1}1]$, $[\bar{1}01]$ and $[\bar{1}\bar{1}0]$ directions. The fine structure and the linear triangular features were also clearly identifiable with the secondary electron technique, and an image of the trihydride film is shown in Figure 7.4. The UFM images of the linear features in the hydrogenated samples showed no material contrast relative to the surrounding material, indicating that the features are a surface corrugation of the same material. The AFM and associated UFM images are shown in Figure 7.5.

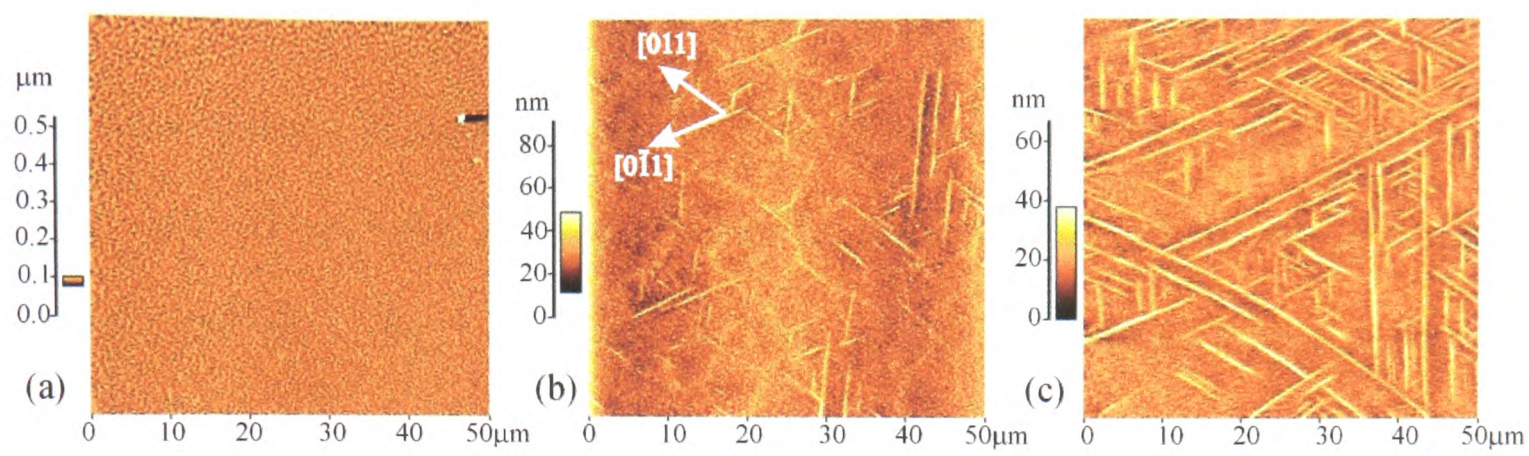


Figure 7.3 : AFM topography of the three samples showing (a) the as-grown metal, (b) the dihydride and (c) the trihydride samples.

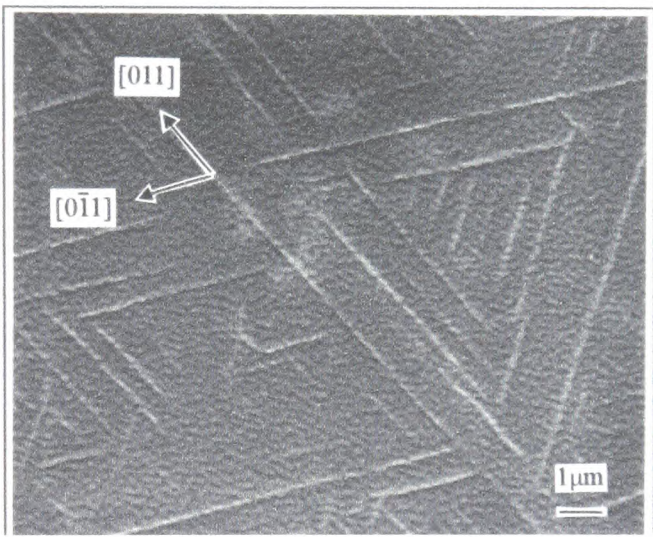


Figure 7.4 : secondary electron image of the trihydride sample clearly showing the triangular ridge features

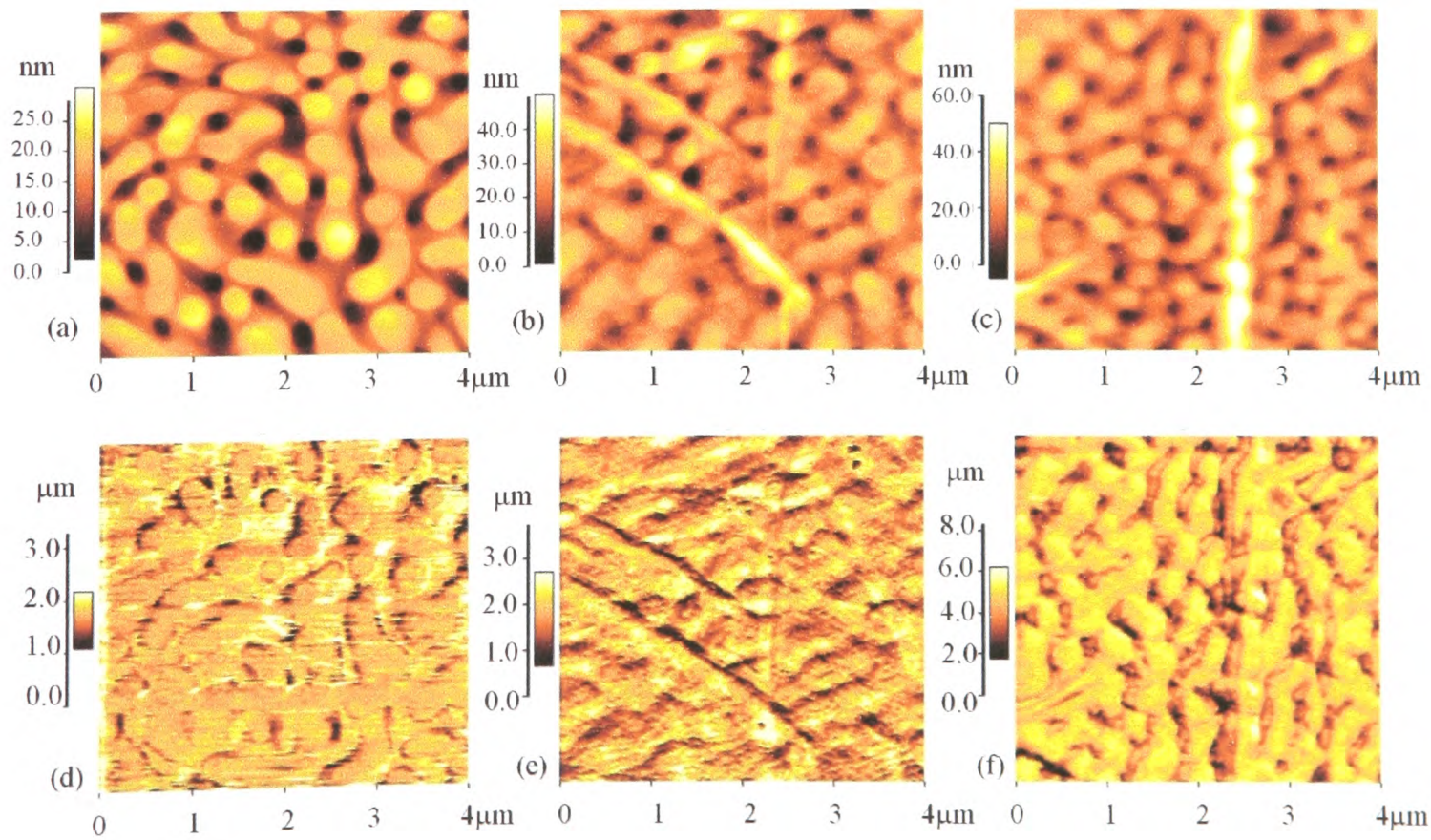


Figure 7.5 : High resolution AFM images of (a) as-grown metal, (b) dihydride and (c) trihydride. The UFM elasticity measurements of the same areas are shown in (d), (e) and (f) respectively

7.3.4 In-situ TEM analysis

The maximum working pressure of H_2 in the in-situ CETEM loading experiments was not sufficient to drive the phase transition from the β -phase to the γ -phase, but significant changes were observed in the crystal structure even within the superstoichiometric β -phase that was achieved. Figure 7.6(a) shows a typical area of the HoH_2 film prior to loading; clearly shown are two twin boundaries that lie discretely in the basal plane. Although there is a unique orientation relationship of the Ho metal when deposited on the Nb buffer, upon transformation to the β -phase there are now two equivalent orientations, and so twins are expected. Interestingly, prior to in-situ H loading the twin boundaries were found to be confined to the (111) twin planes parallel to the substrate. After the loading process twin boundaries were observed out of the plane as well, as shown in Figures 7.7(a) and 7.7(b). Associated with the latter twin boundaries is a characteristic image contrast in which every third plane appears in sharp contrast and the two layers in between have a lower contrast. Figure 7.8(a) shows this characteristic image contrast at higher magnification. To understand electron micrographs, dynamical interactions between diffracted and incident beams must be accounted for, which results in the contrast being highly dependent on specimen thickness and defocus. In order to draw direct conclusions about the crystal structure it is necessary to perform computer simulations for the assumed crystal structure for a number of different thicknesses and defoci, to enable comparison between simulated and experimental images. The software used for the simulations was EMS [16]. The best match between image and simulation is shown in Figure 7.8(b). The model used to generate this image is a crystal in which slip has occurred. The formation of the characteristic image contrast is shown in Figure 7.8(c) and 7.8(d). Figure 7.8(c) shows the projection of a crystal (looking along the [110] zone axis), with a twin boundary in the (111) growth plane, prior to loading. The two twins are clearly indicated as regions A and B.

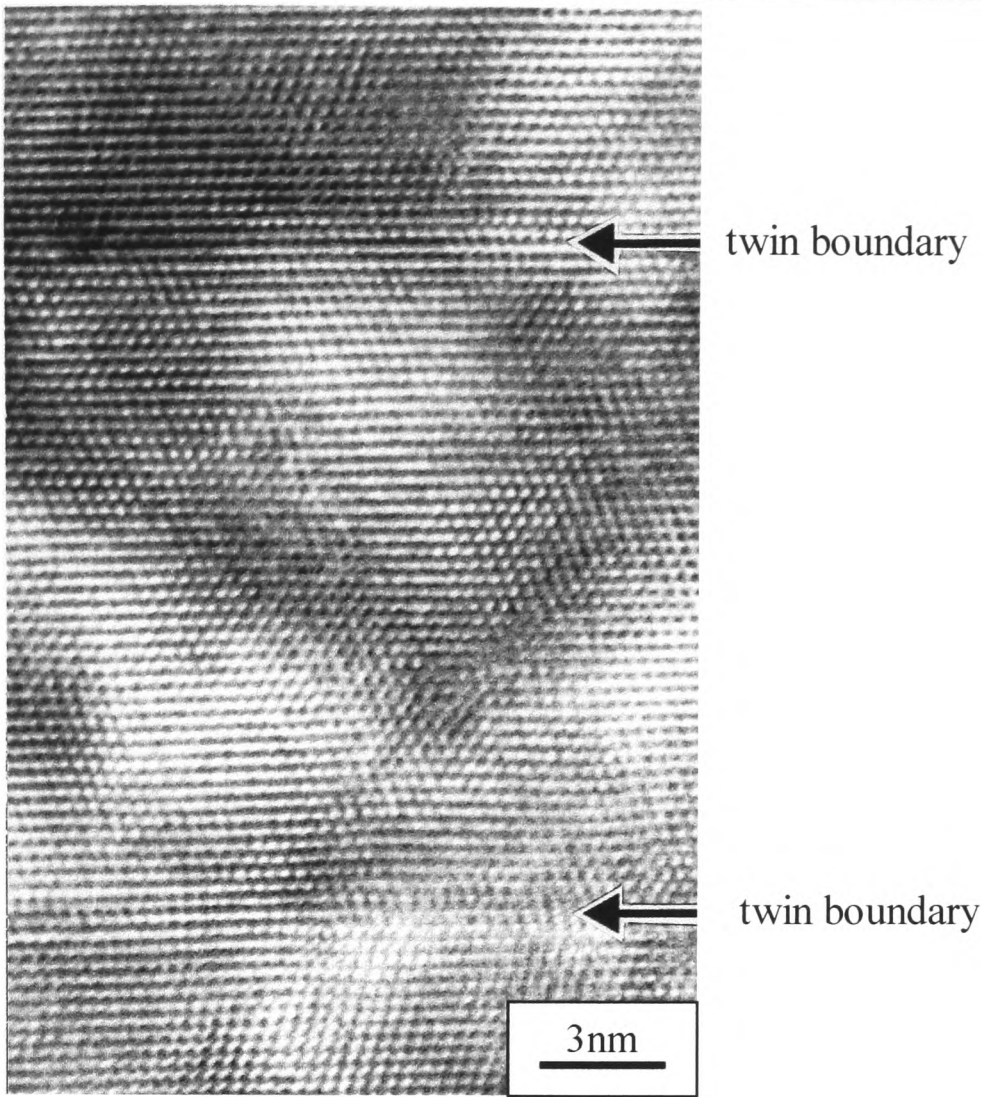


Figure 7.6 : HREM image of HoH₂ layer taken along $[\bar{1}10]$ prior to loading:

the twin boundaries lie discretely in the basal plane

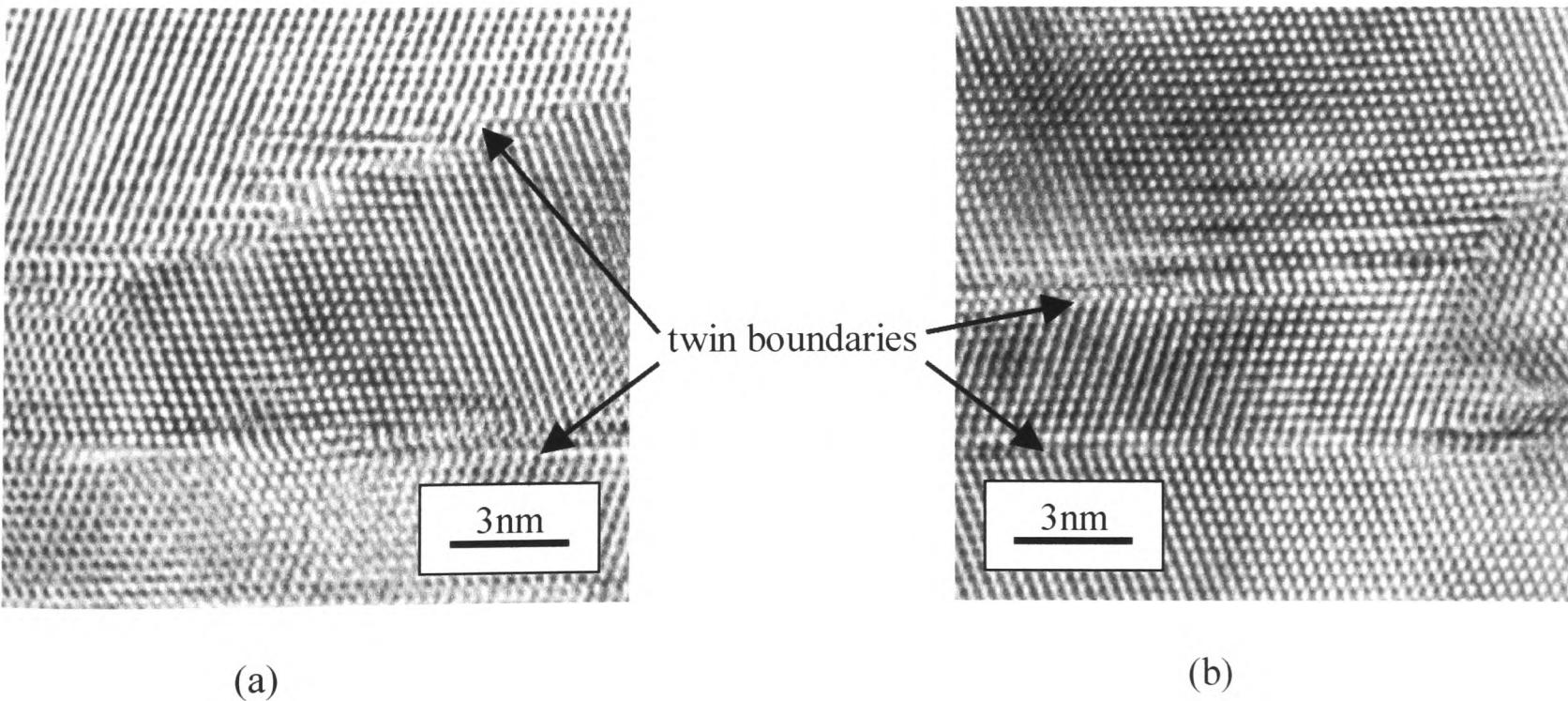


Figure 7.7 : HREM images of HoH₂ layer taken along $[\bar{1}10]$ after loading: the twin boundaries no longer lie discretely in the basal plane, but are inclined to the growth plane. There is also a characteristic contrast associated with the twin boundaries

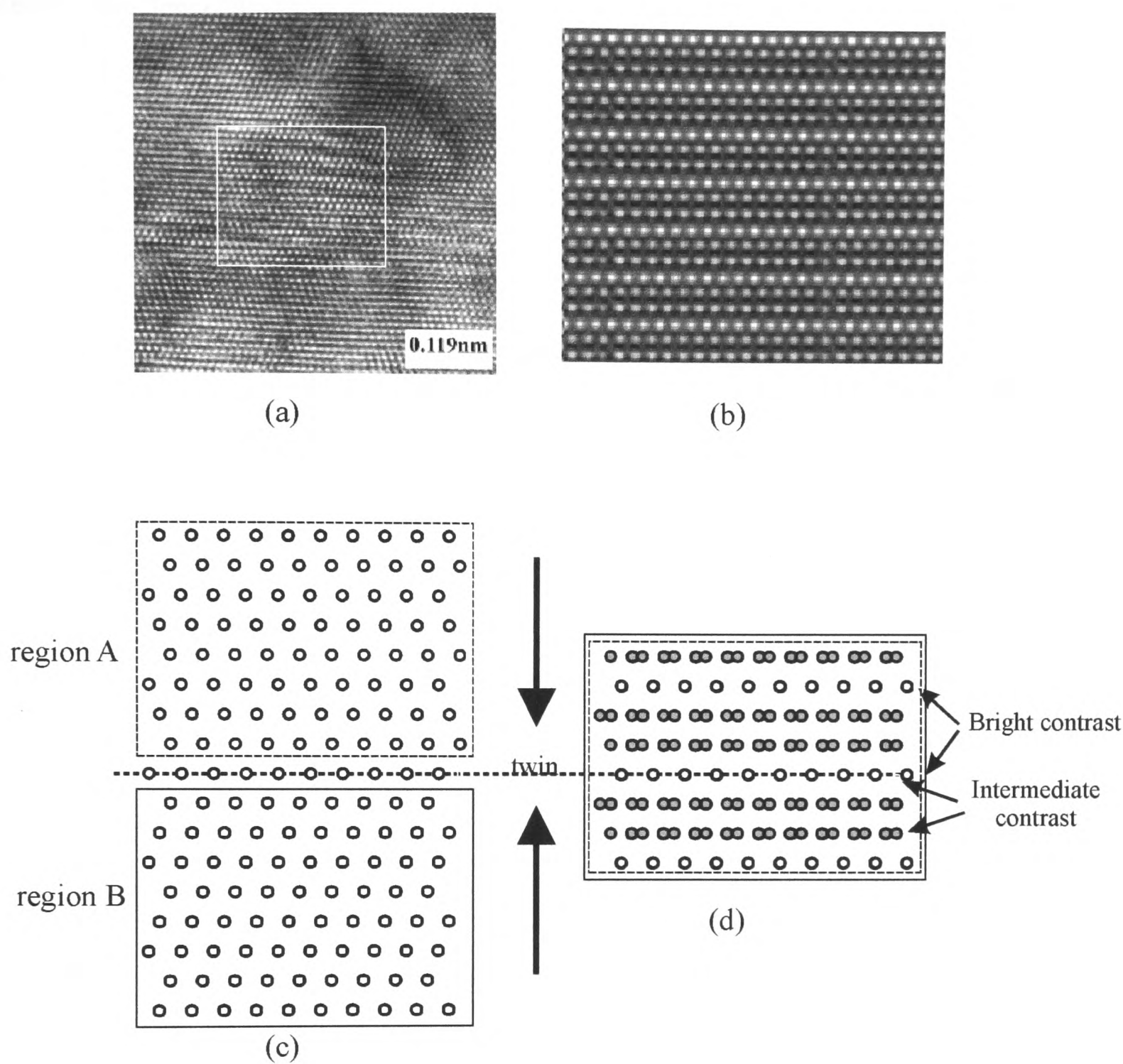


Figure 7.8 : (a) Image of HoH_{2+x} taken along the $[110]$ zone axis. The region inside the white box shows an image contrast in which every third plane appears with bright contrast, the intervening planes with lower contrast. (b) Computer simulation of the image, confirming the proposed slip structure does in fact give this distinctive image contrast. (c) diagram of the image contrast surrounding a twin boundary (marked with dotted line) prior to hydrogen loading. The twins are marked region A, surrounded by a dashed box, and region B, surrounded by a solid box. (d) diagram of the area adjacent to a twin boundary after hydrogen loading; region A and region B have slipped past each other in the directions indicated by the arrows. Looking in projection through a slice of crystal, every third plane aligns perfectly (bright contrast) with the intervening two layers being slightly displaced from one another (lower contrast).

Before slip, the columns of atoms, which are viewed in projection in an HREM image belong discretely to one twin. Figure 7.8(d) shows the projection when regions A and B have slipped past each other in the directions indicated by the arrows. Thus after slip has occurred, the atom columns in the projection of the specimen consist of a mixture of the two twins. As the stacking of planes in a cubic crystal is ABCABC..., if an equivalent twin slips (CBACBA...), assuming that the slip occurs over an integral number of growth planes, every third plane will be in perfect alignment (high contrast) with the two intervening planes not perfectly aligned (lower contrast).

7.4 Discussion

The above analysis has confirmed the introduction of structural defects as epitaxial Ho films are loaded with hydrogen, including β -phase twins, slip and the formation of macroscopic features (ridges) in a triangular pattern on the surface. It is interesting that similar triangular features were reported by Nagengast *et al.* [11] for Y films on CaF_2 ; thus these features appear to be a general occurrence following H loading of (0001) rare earth films irrespective of which substrate system is employed. Nagengast *et al.* [11] attribute the triangular ridges to material being "squeezed out of the surface as a result of (i) in-plane thermal expansion differences of the substrate and film, and (ii) in-plane expansion of the Y lattice during H absorption". In our case the thermal expansions of substrate (sapphire) and film are well matched, so that suggestion (i) does not apply. Instead we attribute the ridge formation to precipitation of the β - and γ -phases in turn within the host lattices, the α - and β -phases respectively. Very similar features have been observed in the Nb-H system by Birnbaum *et al.* [17]. Note that in our case the features cannot be a result of the hydrogen loading of the Nb cap, as the height of the features is between 2 and 3 times the thickness of the Nb, but we propose a similar effect taking place in the Ho-H system. In each case the

lattice of the precipitating phase is significantly expanded with respect to the host lattice. As shown in Figure 7.2, this volume expansion is 8.7% and 10.5% respectively at the two phase changes in the Ho-H system (cf. 12% in Nb-H [17]). There is an additional constraint on the accommodation of this expansion because of epitaxial clamping in the plane of the sample. As a result it is likely that the initial nucleation and growth of the precipitating phase will take place along inclined slip planes of the host lattice, leading to material being forced out of the surface in ridges which denote the edges of the precipitating plates. Therefore the ridges are aligned along the intersections of inclined slip planes with the surface plane. Note that stresses resulting from the precipitation process will certainly cause slip of the host lattice, but slip may already be present as a result of stresses accompanying H dissolution in the α -phase and may then provide precipitate nucleation sites. The evidence of the CETEM analysis supports this model, in that slip is observed to occur in the superstoichiometric β -phase prior to precipitation of the γ -phase. Note that in the case of HoH_{2+x} , it is the contraction of the lattice as the hydrogen concentration increases above $x=0$ which leads to slip. Birnbaum *et al.* [17] found that the precipitation effects in Nb-H were irreversible and that during repeated cycling, precipitation took place preferentially at the same features. In the present case we likewise suppose that the plastic deformation effects because of precipitation are retained throughout further loading/unloading operations.

The predominant slip planes of the hcp α -phase are $(10\bar{1}0)$ type [18], which intersect the (0001) surface plane along $\langle 11\bar{2}0 \rangle$ directions, as observed for the linear features. These are shown in Figure 7.9 (a). In the fluorite β -phase system at room temperature the predominant slip planes are $\{001\}$ [19] with the Burgers vectors being the $\frac{1}{2}\langle 110 \rangle$ type. The intersections of these slip planes with the $(111)_{\text{fcc}}$ surface plane are along the $\langle 110 \rangle$ directions, as shown in Figure 7.9 (b). At higher temperatures the $\{110\}$ and $\{111\}$ planes

become possible slip planes, and the intersections of these planes with the $(111)_{\text{fcc}}$ growth plane are also along $\langle 110 \rangle$. Therefore, the orientation of the observed triangular features is consistent with the hypothesis that they are a result of precipitation in slip planes of the host lattice. In addition, the AFM images reveal larger concentrations of triangular features on the surface of the trihydride, consistent with their formation at both the phase changes involved in loading to the trihydride. In this model the density of such features will be a function of the rate of hydrogen dissolution and precipitation at each phase change. In contrast to these results the work of Kerssemakers *et al.* find that such ridges form in YH_2 films on CaF_2 substrates at the α - β phase transitions and that the ridge network remains unchanged through further cyclic (un)loading between YH_2 and YH_3 . Subsequent work using similar substrate systems and rare earth layers would be of great interest to investigate the different observations of the two groups.

A final discussion point concerns the proposed formation of epitaxial Ho_2O_3 as a minor component of the trihydride sample. This could arise because of the reaction with residual water vapour or (less likely) oxygen during loading, or by subsequent reaction in air. It is known that the ageing process of the heavy rare earth metals involves the reaction with water vapour to form the dihydride [18] and then further reaction to eventually form the sesquioxide, which is thermodynamically by far the most stable compound. This process is accelerated by heating to temperatures around 100°C , but is also very sensitive to the nature of the capping layer used. If no capping layer is deposited on the rare earth then a thin epitaxial oxide layer forms which effectively inhibits further reaction at room temperature, whereas if Pd or Au capping layers are employed to facilitate fast H-cycling then the ageing process in air is accelerated. In the present case, the fact that the XRD pattern has remained unchanged since the first examination of the trihydride sample after loading suggests that in

the present case the oxide component formed by reaction with trace quantities of water vapour during H loading.

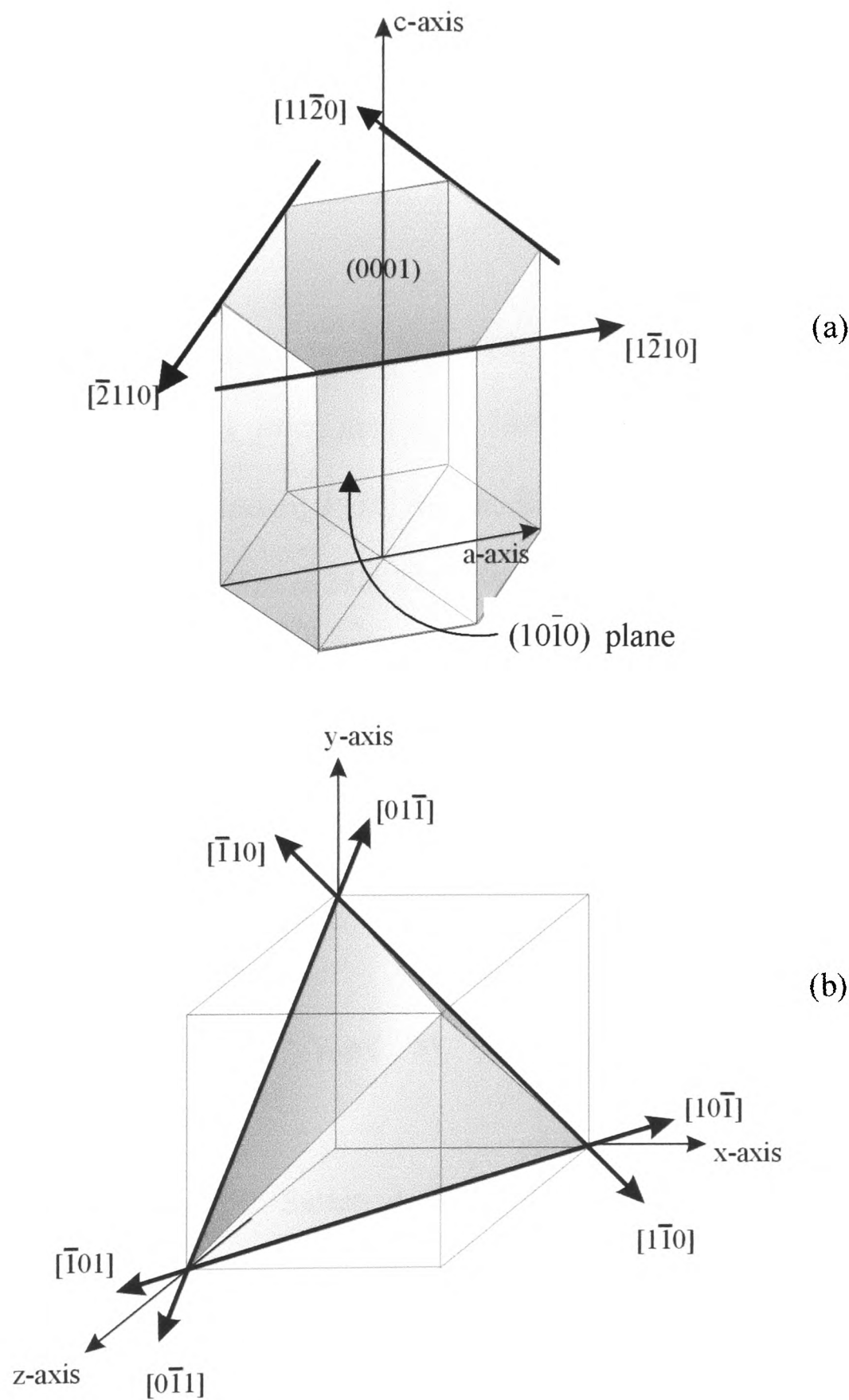


Figure 7.9: (a) Intersection of the {1010} slip planes with the (0001) growth plane in the α -phase metal, (b) Intersection of the {111} slip planes with the (111) growth plane in the β -phase dihydride. The intersections are indicated with a heavy black line

References

- [1] P. Vajda "Hydrogen in rare-earth metals, including RH_{2+x} phases", in *Handbook on the physics and chemistry of rare earths*, Vol. 20, edited by K. A. Gschneidner Jr. and L. Eyring, Elsevier Science, 208 (1995).
- [2] G. Andre, O. Blaschko, W. Schwarz, J. N. Daou, and P. Vajda, *Phys. Rev. B* **46**, 8644 (1992).
- [3] P. Vajda and J. N. Daou, *Z. Phys. Chem.* **179**, 443 (1993).
- [4] J. N. Daou and P. Vajda, *Phys. Rev. B* **45**, 10907 (1992).
- [5] J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, *Nature* **380**, 231 (1996).
- [6] P. van der Sluis, *Appl. Phys. Lett.* **73**, 1826 (1998).
- [7] F. J. A. den Broeder, S. J. van der Molen, M. Kremers, J. N. Huiberts, D. G. Nagengast, A. T. M. van Gogh, W. H. Huisman, N. J. Koeman, B. Dam, J. H. Rector, S. Plota, M. Haaksma, R. M. N. Hanzen, R. M. Jungblut, P. A. Duine, and R. Griessen, *Nature* **394**, 656 (1998).
- [8] A. R. Wildes, R. C. C. Ward, M. R. Wells, and B. Hjorvarsson, *J. Alloys and Compounds* **242**, 49 (1996).
- [9] A. Remhof, G. Song, C. Sutter, A. Schreyer, R. Siebrecht, and H. Zabel, *Phys. Rev. B* **59**, 6689 (1999).
- [10] J. Hayoz, S. Sarbach, T. Pillo, E. Boschung, D. Naumovic, P. Aebi, and L. Schlapbach, *Phys. Rev. B* **58**, R4270 (1998).
- [11] D. G. Nagengast, J. W. J. Kerssemakers, A. T. M. van Gogh, B. Dam, and R. Griessen, *Appl. Phys. Lett.* **75**, 1724 (1999).
- [12] J. W. J. Kerssemakers, S. J. van der Molen, N. J. Koeman, R. Gunther, and R. Griessen, *Nature* **406**, 489 (2000).

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- [13] O. V. Kolosov, *Materials World* 753 (1998).
- [14] G. v. Brauer and R. Hermann, *Zeitschrift für anorganische und allgemeine Chemie. Band 274*, 11 (1953).
- [15] L. Z. Mezey and J. Giber, *Jap. J. Appl. Phys.* **21**, 1569 (1982).
- [16] P. A. Stadelman, *Ultramicroscopy* **21**, 131 (1987).
- [17] H. K. Birnbaum, M. L. Grossbeck, and M. Amano, *J. Less-Common Metals* **49**, 357 (1976).
- [18] H. K. Smith, A. G. Moldovan, R. S. Craig, W. E. Wallace, and S. G. Sankar, *J. Solid State Chem.* **32**, 239 (1980).
- [19] A. Kelly and G. W. Groves *Crystallography and crystal defects*, Longman, London, 175 (1970).

Chapter 8

Determination of hydrogen ordering within the β -RH_{2+x} phase (R-Ho, Y) using electron diffraction techniques

Chapter 8 presents the results into an investigation into the ability of electron diffraction techniques to detect hydrogen ordering within RH_{2+x} systems. Section 8.1 explains why such an investigation was undertaken, with sections 8.1.1 discussing the effects that hydrogen ordering can have on a system, 8.1.2 detailing the hydrogen superstructures already observed in metal-hydride systems and 8.1.3 discussing three different diffraction techniques namely neutron, x-ray and electron diffraction and their suitability to study hydrogen ordering in metal-hydrides. Section 8.2 explains the theory used to calculate the diffraction patterns, and presents the structures that considered in this work. Finally section 8.3 presents the results of computer simulations of electron diffraction patterns and discusses the usefulness of using this diffraction technique in the investigation of these structures.

8.1 Introduction

As part of the study of rare earth metals and hydrides high resolution electron microscopy, HREM, has been used as a characterisation tool. As discussed in chapter 6, the rare earths are extremely reactive, and conventional specimen preparation techniques [1] have not proved successful for producing specimens representative of the as-grown metal films, and instead many of the specimens are observed to exhibit a range of structures including the RH₂ phase. However it has been shown that it is possible to prepare TEM samples representative of the α -phase using a focused ion beam system.

A typical diffraction pattern from a conventionally prepared TEM specimen from a holmium metal film is shown in Figure 8.1. The diffraction pattern shows no evidence of the original hcp metal structure, but instead the films now exhibit a range of crystallographic

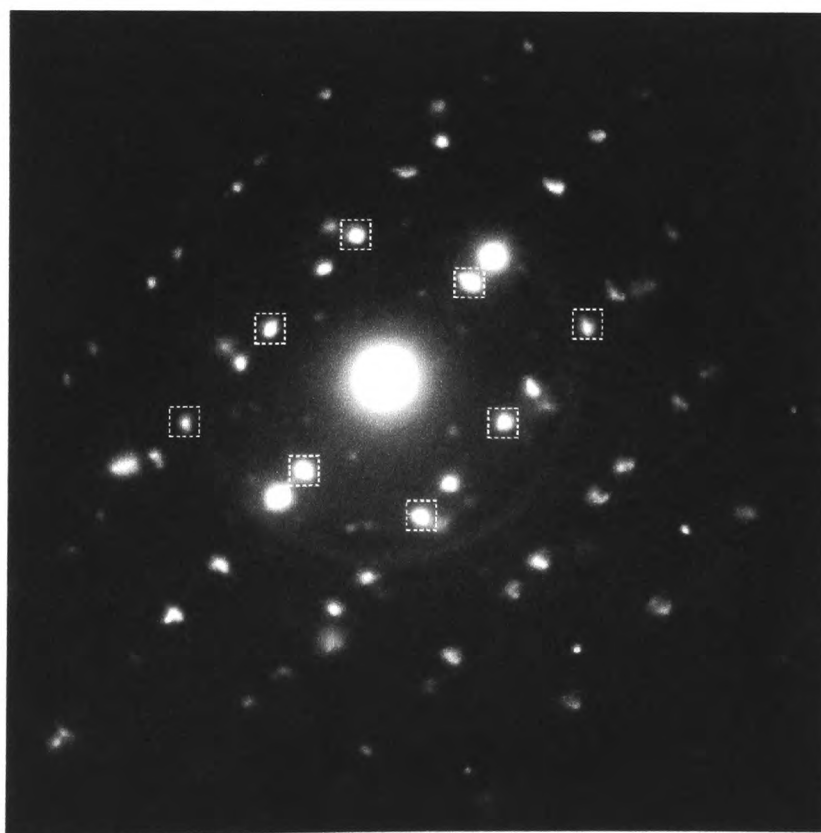


Figure 8.1: A typical electron diffraction pattern from a conventionally prepared rare earth sample, viewed along a [110] projection. The fcc metal-hydride lattice spots are marked with dashed boxes (the twin structure is not marked but is easily identifiable).

The pattern is obviously complex, and the original material (in this case holmium

metal, hcp) has been changed during preparation.

structures including the RH₂ and R₂O₃ phases. It is thought that such reactions occur during the final stage of specimen preparation, when the samples are cooled to liquid nitrogen temperatures under vacuum and are milled by a beam of Ar atoms; during this process the samples can react with the residual water vapour within the chamber to form hydrides, hydroxides and oxides. However even after the identification of the dihydride and oxide phases there are other unidentified structures present in the diffraction pattern and it was important to uniquely identify as many as possible of the crystal species present, particularly for the work presented in the previous chapter on the hydrogen induced deformation of epitaxial (0001) holmium films.

As can be seen in the phase diagram, the β -phase dihydride exists over a considerable range of hydrogen concentration and in the range RH_{2+x} the excess H atoms are effectively in solution in the octahedral interstitial sites of the fcc dihydride lattice and are free to interact with each other and form hydrogen sublattices [2]. This ordering has been observed as anomalies in several physical properties [3,4]. As part of the wider study to identify uniquely the phases present within such specimens, computer simulations of the diffraction patterns from hydrogen ordered structures were performed. The fact that the presence of hydrogen ordered structures did significantly alter the electron diffraction patterns was unexpected, as at first thought it may be assumed that the presence of such a light element in a heavy metal lattice would have little effect. The computer simulations ruled out the presence of hydrogen ordering within the samples studied, namely those which had hydrogenated during sample preparation, but opened up the possibility for using this technique with samples deliberately loaded to specific H-concentrations. All previous investigations of such structures have used neutron diffraction techniques, and have not always proved successful, for reasons which will be discussed later in this chapter. The computer simulations and comparison of the diffracted intensities for the electron, neutron

and x-ray cases shows that electron diffraction is a viable and hitherto overlooked technique for studying hydrogen ordering in these systems.

8.1.1 The effect of ordering within the β -RH_{2+x} phase

In the range RH_{2+x} the excess H atoms are effectively in solution in the RH_{2+x} lattice with the excess hydrogen atoms occupying the octahedral sites (*o*-sites) within the unit cell. When the structures are cooled below their mobility limits, the octahedral hydrogens atoms can form short-range ordered (SRO) and long-range ordered (LRO) structures. At higher temperatures the RH_{2+x} system may be considered as a lattice gas in which the excess hydrogen atoms randomly occupy the octahedral interstices of the fcc lattice. The temperatures at which this ordering occurs for a given value of hydrogen concentration is independent of rare earth atom, for example the ordering has been observed at 150K for YH_{2.05} and HoH_{2.065}, and at 200K for YH_{2.1} and 240K for HoH_{2.14} [4,5]. The difference between the rare earth atoms is exhibited as a diminishing solubility limit in the β -phase, $x_{\beta}^{\max}$, as a result of the lanthanide lattice contraction. The ordering has been observed to give rise to anomalies in many of the physical parameters. For example, the first indication of ordering within the heavy rare-earth systems is shown by resistivity anomalies in the β -TbH_{2+x} system [6]. In LaH_{2+x} [7] and CeH_{2+x} [8] the ordering can give rise to a tetragonal distortion of the cubic unit cell. In GdH_{2+x} the ordering is seen as anomalies in the thermal behaviour of the lattice parameter [9]. The lattice parameter of the dihydride decreases with increasing hydrogen content because of the ionic nature of the bonding, but it was seen that this contraction was stronger at lower temperatures, and deviated from linearity, indicating interaction between the octahedral hydrogens leading to eventual ordering.

The ordering has also been connected with the eventual metal-insulator, M-I, transition that occurs in these systems. An M-I transition has been observed in the slightly superstoichiometric dihydride YH_{2.1} [10] upon cooling which implies that an order-disorder transformation in the direct hydrogen octahedral sublattice drives the transition. In contrast it was the order-disorder transition within the octahedral vacancies which was the mechanism proposed for the M-I transition in the hydrogen rich CeH_{2+x} (0.7<x<0.8) and LaH_{2+x} (0.8<x<0.9) systems, where the breakdown of the octahedral vacancy lattice leads to a breakdown of a delocalised carrier band which is supposed to drive the M-I transition.

The ordering of the excess hydrogen atoms will obviously also affect the magnetic properties of a material. It is generally observed in the heavy rare-earths that there are several magnetic ordering transitions (even within the pure dihydrides) but in the superstoichiometric dihydrides these are emphasized by the presence of both commensurate and incommensurate magnetic phases that are strongly influenced by modifications to the crystal field symmetry and the Fermi surface as a result of the excess H atoms [3].

The fact that physical properties are very dependent on hydrogen concentration and structure means that it is very important to understand the way in which the structure changes with increasing hydrogen concentration. This study looks at the different roles that electron, x-ray and neutron diffraction techniques can play in characterising these changes.

8.1.2 Ordered structures in rare earths and other metal systems

In CeD_{2+x}, for which the D atoms are continuously soluble up to the trihydride, different deuterium ordered structures (I4₁/m and I4/mmm) have been observed as a function of concentration by neutron scattering [11,12]. No isotope effect is assumed. André et al. [2] showed that the excess deuterium in TbD_{2+x} (0.1≤x≤0.2) orders in a DO₂₂ (Ni₃Mo) structure. NiMo and Ni₄Mo ordering in which every other (z=0.5) and every fifth (z=0.8)

(420) planes are empty have been observed in PdD_z [13]. LaH_{2+x} orders in a Ni₄Mo state ($x=0.8$) [7]. The ordering in CeH_{2+x}, LaH_{2+x} and TbD_{2+x} can be described by ordering on the (420) planes (for example, the Ni₄Mo ordered structure of LaH_{2+x} corresponds to four consecutive (420) planes with filled *o*-site hydrogen followed by a fifth plane with all *o*-sites vacant), and this ordering can be characterised by the wave vector $[1, \frac{1}{2}, 0]$.

8.1.3 Diffraction Techniques

The ordered structures in all the rare-earth systems described above have been identified using neutron scattering techniques, with the exception of the LaH_{2+x} system. The cubic to tetragonal distortion in LaH_{2+x} was studied using x-rays, and the results led Klavins *et al.* to propose the Ni₄Mo ordered structure as the best explanation of the results. Neutron diffraction is obviously an important tool in determining the position of light atoms within crystals containing heavy atoms, as the interaction of neutrons is not linearly dependent on atomic number, *Z*. However, the characterisation of the HoH(D)_{2+x} ordered structure with neutrons failed [14], despite strong indications towards such an ordering from anomalies in the electrical resistivity and in the change in lattice parameter with temperature. The failure of the neutron method to characterise the structure was thought to be either because the deuterium concentration was too low, or the long-range order of the superstructure was not developed enough to be detectable.

Of the other diffraction techniques X-rays have a scattering amplitude proportional to *Z*, because they are scattered from the electron charge cloud surrounding an atom. Thus x-rays are not sensitive to light atoms bound within a heavy metal lattice. However Electrons interact strongly with crystals as they are scattered from the nucleus as well as from the outer electrons, and at small angles the scattering factors for electrons are of order 10^4 times greater than x-ray scattering factors, but so far there do not appear to have been

any attempts to use electrons in characterising these structures. In comparison to the neutron studies of thin films, where the samples required are large and the results of an investigation show the average across the whole sample, electrons are able to characterise relatively small areas of a material, and thus the lack of long-range order would be overcome with electron diffraction techniques. This combined with the relatively large scattering amplitudes means that electrons are ideally suited for detecting H-ordered structures.

8.2 Theory

8.2.1 The structures considered for this study

In general, for the H-ordering to occur, there must be an accompanying decrease in the total energy of a system. Thus to determine whether or not a state is stable it is necessary to assume an "intuitive" subset of possible crystal structures and compare the total-energy-versus-volume curves for the set to find the most stable structure. This method can be successful, but depends upon the ability to guess a canonical set of structures which includes the minimum energy configuration. In order to determine whether or not it was possible to detect hydrogen ordering within the β -phase by electron diffraction it was necessary to determine firstly the range of concentrations in which this ordering might occur, and secondly the possible structures that the system might adopt within this range. Experiments on TbD_{2+x} compounds performed within the concentration range $0.095 \leq x \leq 0.18$ found the ordering to be the DO₂₂ structure (corresponding to $x=0.25$). This, together with the fact that experimental data available for hydrogen ordering within the YH_{2+x} and HoD_{2+x} systems are for concentrations ranging between $0 \leq x \leq 0.19$ [4] and $0 \leq x \leq 0.14$ respectively, means that it seems reasonable that physically realistic ordered systems will lie between $0 \leq x \leq 0.25$. (Even

if the actual concentration were somewhat lower, the ordering could still correspond to the ideal concentration of $x=0.25$).

Sun et al. [15] used a subset of suitable fcc structures for the β -YH_{2+x} system for their work on first-principles total energy calculations of the phase stability of the ground state configurations. Although their work ignored the fact that for $x\geq 0.1$ YH_{2+x} undergoes a structural phase change, to a mixture of fcc and hcp, the subset is ideal for the present study as it considers all the possible orderings that can occur within the cubic phase. This work uses the systems considered by Sun et al. within the concentration range $0\leq x\leq 0.25$. These structures are summarised in Table 8.1, and are shown in Figure 8.2.

name	fcc	D1	D1 _a	D0 ₂₂
(100) projection				
Space Group	Fm $\bar{3}$ m	Fm $\bar{3}$ m	I4/m	I4/mmm
X (concentration)	0	0.125	0.2	0.25

Table 8.1 - Large circles represent the top (100) plane sites, and small circles the sites of the adjacent plane shifted by $a/2$ relative to the top plane. Solid and hollow circles are the occupied and empty sites respectively. All except D1 are invariant under translation of a in the (100) direction. D1 has a translational periodicity of $2a$ in the (100) direction. The complete circles represent that the occupation by H is on the top (100) planes and the strongly outlined circles represent that the occupation by H is on the plane shifted away from the top plane in the (100) direction by a .

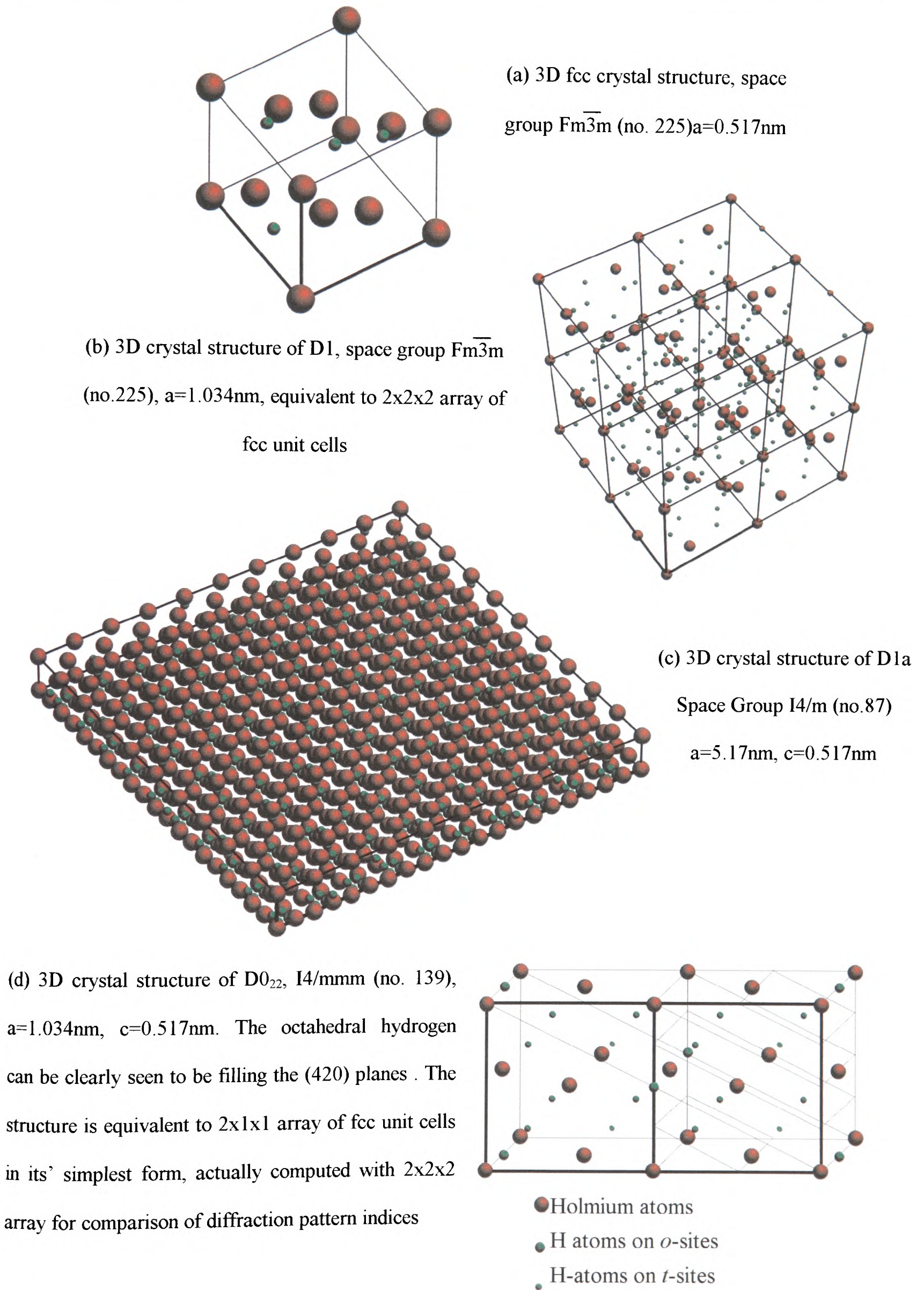


Figure 8.2: The 3-D crystal structures, showing only the unit cells for each of the structures

The intensity in the diffracted beam was calculated using the basic theory outlined in section 4.1.2.1, where it was shown that the structure factor for the whole unit cell is given by

$$F = \sum_{j=1}^n \sum_{i=1}^m f_j(\mathbf{g}) \mathbf{e}^{2\pi i[\mathbf{g} \cdot \mathbf{r}_i]} \quad (8.1)$$

where j is the sum over atom types and i is the sum over atom positions. This is completely general and can be applied to all crystal lattices. In order to calculate the intensity of the beams at the exit surface of a specimen, and hence the diffraction pattern, the image simulation software EMS [16] was used.

8.3 Results and Discussion

The calculated diffraction patterns are shown in Figure 8.3. For direct comparison of the patterns it is necessary to adjust the indices relative to the unit cells shown in Figure 8.2, i.e. the (440) spot on the pattern shown in Figure 8.3(b) is equivalent to the (220) spot in the fcc pattern as the unit cell is 2x2x2 standard fcc cells. In the figure the spot size is proportional to the intensity in the beam.

Figure 8.3(a) shows the diffraction pattern obtained from the stoichiometric crystal HoH_{2.0} viewed along the $[\bar{1}10]$ zone axis. Although the crystal has the fcc fluorite structure, the diffraction pattern is not affected by the hydrogen atoms lying on the tetrahedral (t) sites, but shows the standard $[\bar{1}10]$ symmetry formed by electron diffraction from the fcc lattice of metal ions. Figure 8.3(b) is the $[\bar{1}10]$ diffraction pattern of the D1 structure. The strong spots shows the same basic fcc diffraction symmetry (with (440)_{D1} equivalent to (220)_{fcc}), but there are also extra, weak spots at the (111), (002) and (220) positions. Figure 8.3(c) is the $[\bar{1}10]$ diffraction pattern of the D1_a structure. Again the basic fcc symmetry from the fcc

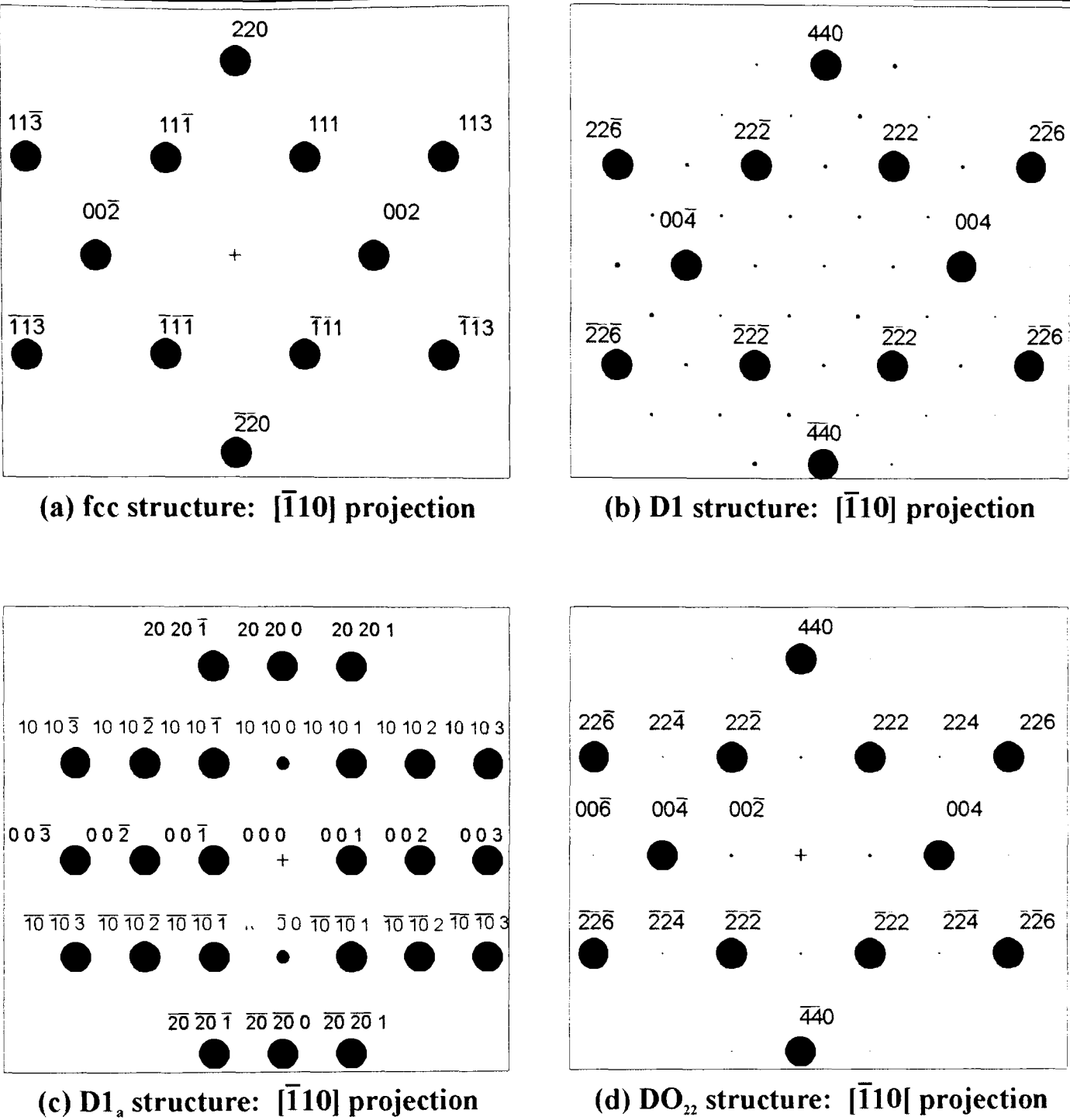


Figure 8.3: Calculated diffraction patterns for the various ordered structures shown in Figure 8.2

metal ion lattice is evident (with $(20,\bar{2}0,0)_{D1_a}$ equivalent to $(\bar{2}20)_{fcc}$) but extra spots can also be seen at $(10,\bar{1}0,0)_{D1_a}$ and at $(001)_{D1_a}$. Although the $(001)_{D1_a}$ spots can be seen to have a slightly weaker intensity than the majority of the other spots, the $(10,\bar{1}0,0)_{D1_a}$ type positions have the same relative intensity as the "fcc" spots. Figure 8.3(d) is the $[\bar{1}10]$ diffraction pattern of the DO₂₂ structure. Along with the basic fcc pattern extra, weak spots can be seen at $(002)_{DO_{22}}$ and $(\bar{2}20)_{DO_{22}}$ with considerably less intensity than the main spots.

All the ordered structures thus show extra peaks at the $(001)_{fcc}$ and $(110)_{fcc}$ type positions, with structure D1 also showing extra peaks at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})_{fcc}$. Simulations of the

structures with randomly distributed hydrogen atoms showed no extra reflections. Significantly, these extra peaks cannot be attributed to dynamical scattering events. When the scattering is dynamical each spot in the diffraction pattern acts as a new incident beam, and the position of new peaks can be inferred by adding the existing diffraction pattern at these positions. This does not generate peaks at the {001} and {110} positions. We can conclude therefore, that the extra peaks are a result of the presence of ordered hydrogen within the system and that they must be arising from kinematic scattering events. As x-ray scattering is also mainly kinematical, such peaks would also be present in x-ray diffraction experiments, the issue in these experiments being whether or not there is sufficient intensity in the extra peaks for them to be detected.

The ratio of the intensity of the superlattice spots to the (111) allowed reflection, using the theory outlined in section 4.1.2.1, with values for the electron and x-ray scattering factors and neutron scattering lengths taken from the International Tables for Crystallography [17] [18] [19] is shown in Table 8.2. The scattering factors used were those for neutral atoms. The model of the electronic state of hydrogen in the rare earths is complicated, however in the β -phase the material is still metallic, albeit with metallic properties significantly diminished from the α -phase, and thus the best approximation for the scattering is to use the values for neutral ions.

	electrons	x-rays	neutrons (H)	neutrons (D)
$\frac{I(110)_{D0_{22}}}{I(111)_{D0_{22}}}$	1.74×10^{-4}	8.577×10^{-6}	1.00×10^{-2}	5.59×10^{-2}
$\frac{I(001)_{D0_{22}}}{I(111)_{D0_{22}}}$	2.46×10^{-4}	1.331×10^{-5}	1.00×10^{-2}	5.59×10^{-2}

Table 8.2 - comparison of the intensity in the (001) and (110) diffraction peaks, relative to the (111) diffraction peak, for electrons x-rays and neutrons

Table 8.2 suggests that neutrons should be the best tool for detecting hydrogen ordering, with only a factor of 10^2 (less for deuterium) between the allowed fcc peaks and the extra spots due to hydrogen ordering. This is because the scattering amplitude is not linearly dependent on Z and so hydrogen does not have a weak scattering amplitude when compared to the host metal. However, as already mentioned, neutrons are not successful at characterising the structures when the hydrogen concentration is too low, or the long-range order of the superstructure is not developed enough to be detectable.

The values in Table 8.2 show that the ratio of the superlattice to primary peaks in the x-ray case is significantly smaller than it is for electrons, indeed at small angles the scattering factors for electrons are of order 10^4 times greater than x-ray scattering factors. It is important to note that in both cases the scattering is kinematical and thus the intensity in the primary beam is not diminished by additional scattering events. If dynamical scattering (i.e. the beam suffers more than one scattering event as it passes through the sample thickness) was present in the electron case then multiple scattering events could significantly alter the intensity in the primary spots, and the relative intensity between the extra spots and primary spots would be expected to be enhanced even further.

Although there is a significant difference in intensity between the extra reflections as calculated for both x-rays and electrons, the difference in detection ability in fact lies more in the instruments used for the diffraction experiments themselves. The high count rates associated with electron diffraction experiments can significantly improve the ability to detect the ordered structures. The count rate in a high resolution x-ray source in the laboratory is of the order of 30000 s^{-1} , whereas for an electron microscope operating at 400 kV, the current density on the screen is approximately 150 pA cm^{-2} , and so the count rate is approximately $3 \times 10^{11} \text{ s}^{-1}$. Therefore the electron beam under the conditions used is a factor of approximately 10^7 more intense, and this explains why these weak reflections are

observed by electrons and not by x-rays. Another significant advantage of electrons is that the diffraction data is collected in parallel mode, whereas for both neutrons and x-rays the data is collected in serial mode. Thus to collect a similar signal intensity using x-rays, prohibitively large counting times would be involved. It should be possible to detect such reflections using higher flux x-ray sources, such as the ESRF, however the use of such sources is expensive and limited.

The diffraction patterns were calculated for the $[\bar{1}10]$ zone axis, as it is specimens with this orientation that first stimulated an interest in this problem. Other zone axes would also reveal different sets of extra spots, which disclose more about the symmetry of the structure. However as the purpose of these calculations was to investigate whether or not hydrogen ordering was detectable with electron diffraction, and not a detailed investigation of the symmetry of these structures, these calculations have not yet been performed.

8.4 Conclusions

Ordering within the β -RH_{2+x} phase can be seen in electron diffraction patterns, where similar ordering would not be detected by conventional x-ray sources. The ordered structures all produced extra peaks, which are a result of kinematical scattering events only, at $(001)_{\text{fcc}}$ and $(110)_{\text{fcc}}$ type positions, with structure D1 also showing extra peaks at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})_{\text{fcc}}$, as seen along the $[\bar{1}10]$ zone axis. The extra peaks were not seen for structures where the excess hydrogen atoms were randomly distributed on the octahedral sites. These simulations show that electron diffraction should be considered as a viable alternative to neutron diffraction for studies of hydrogen ordering and indeed may be superior in cases of limited sample volume, for example epitaxial thin films.

References

- [1] S. B. Newcomb, C. B. Boothroyd, and W. M. Stobbs, *J. Mic.* **140**, 195 (1985).
- [2] G. André, O. Blaschko, W. Schwarz, J. N. Daou, and P. Vajda, *Phys. Rev. B* **46**, 8644 (1992).
- [3] P. Vajda and J. N. Daou, *Z. Phys. Chem.* **179**, 443 (1993).
- [4] J. N. Daou and P. Vajda, *Phys. Rev. B* **45**, 10907 (1992).
- [5] J. N. Daou and P. Vajda, *Phys. Rev. B* **50**, 12635 (1994).
- [6] P. Vajda, J. N. Daou, J. P. Burger, and A. Lucasson, *Phys. Rev. B* **31**, 6900 (1985).
- [7] P. Klavins, R. N. Shelton, R. G. Barnes, and B. J. Beaudry, *Phys. Rev. B* **29**, 5349 (1984).
- [8] E. Boroch and E. Kaldis, *Z. Phys. Chem. NF* **163**, 117 (1989).
- [9] M. Chiheb, J. N. Daou, and P. Vajda, *Z. Phys. Chem.* **179**, 271 (1993).
- [10] P. Vajda and J. N. Daou, *Phys. Rev. Lett.* **66**, 3176 (1991).
- [11] A. K. Cheetham and B. E. F. Fender, *J. Phys. C* **5**, L35 (1972).
- [12] C. G. Titcomb, A. K. Cheetham, and B. E. F. Fender, *J. Phys. C* **7**, (1974).
- [13] O. Blaschko, *J. Less-Common Metals* **307**, (1984).
- [14] P. Vajda, G. Andre, and O. J. Zogal, *Phys. Rev. B* **57**, 5830 (1998).
- [15] S. N. Sun, Y. Wang, and M. Y. Chou, *Phys. Rev. B* **49**, 6481 (1994).
- [16] P. A. Stadelman, *Ultramicroscopy* **21**, 131 (1987).
- [17] J. M. Cowley "Section 4.3: Electron scattering", in *International tables for crystallography, Vol. C: Mathematical, Physical and Chemical Tables*, ed. 2., edited by A. J. C. Wilson, Kluwer academic publishers, Dordrecht, (1995).

- [18] E. N. Maslen, A. G. Fox, and M. A. O'Keefe "Section 6.1.1.3: X-ray scattering", in *International tables for crystallography, Vol. C: Mathematical, Physical and Chemical tables*, ed. 2., edited by A. J. C. Wilson, Kluwer academic publishers, Dordrecht (1995).
- [19] V. F. Sears "Section 4.4.4: Scattering lengths for neutrons", in *International tables for crystallography, Vol. C: Mathematical, Physical and Chemical tables*, ed. 2., edited by A. J. C. Wilson, Kluwer academic publishers, Dordrecht (1995).

Chapter 9

Magnetism of HoD_{2+x} single-crystal films ($x=0,0.21$)

Chapter 9 presents an investigation into the magnetic structure of MBE-grown single crystal films of HoD_{2+x} ($x=0,0.21$) using single crystal neutron diffraction techniques. Section 9.1 is a brief overview of the principle interactions which determine the magnetic properties of the rare earths. The section concludes with an overview of the magnetism, as determined by previous experiments using powder samples, in HoD_{2+x} and other rare earth hydride systems. The following section, 9.2, details the growth techniques and experimental procedures employed for the single crystal work. Section 9.4 presents the results first from the stoichiometric sample and then from the superstoichiometric sample. Section 9.5 discusses the results from the two different samples in the light of previous studies on powder samples of HoD_{2+x} .

9.1 Introduction

The magnetic properties of the rare earths have been the subject of many studies over the last few decades because they exhibit such a wide variety of magnetic properties due to the incompletely filled 4f shell. A comprehensive review of the magnetic behaviour of rare earth metals has been written recently by Jensen and Mackintosh [1]. The magnetic

properties of the rare earth hydrides have also been the subject of many studies [2-9] and a comprehensive review of this subject is given by Vajda [10]. However all the experimental results reviewed by Vajda were of measurements performed on powder samples. It is only relatively recently that it was realised that it is possible to obtain single-crystal films grown using MBE techniques, and that such films remain single-crystal even when loaded with hydrogen. This has opened up the possibility of exploiting the single-crystal neutron diffraction techniques employed here to give a much better determination of the magnetic structure, and allowing a better understanding of these systems to emerge.

9.1.1 Rare earth magnetism

In order to understand the magnetism of the rare earth hydrides it is first necessary to consider the magnetic properties of the rare earth elements. In principle it is possible to calculate all observable properties of the atom from the wavefunctions, and so it is first necessary to determine the electronic states of the $4f$ electrons within a rare earth atom. The wavefunction of an electron is determined from the Schrödinger equation

$$H\Psi = E\Psi. \quad (9.1)$$

For an isolated atom, of charge Z , the non-relativistic Hamiltonian operator is

$$H_{\text{int}} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_i \frac{Ze^2}{r_i} \quad (9.2)$$

where m and e are the mass and charge of an electron, and r_i and r_j are the positions of the electrons. The first term in this equation is the kinetic energy of the electrons, the second term is the repulsive interaction between two electrons. The final term is the Coulomb interaction between the nucleus and the electrons. The presence of the two-electron interactions mean that for multi-electron atoms, such as the rare earths, it is impossible to

find exact solutions for this equation, however it is possible to find approximate solutions by using the central-field approximation. In this approximation all the terms in equation 9.2 are replaced by an effective central field, and all non-central interactions between the electrons are then regarded as perturbations to this field. The two most important corrections to the central field are the residual electrostatic interactions and the interactions between the orbital-angular momentum and spins of the electrons. In this scheme,

$$E_{\text{central field}} > E_{\text{residual electrostatic}} \geq E_{\text{spin-orbit}}$$

and it is appropriate to consider the *LS*-coupling approximation in which initially the spin-orbit (*s-o*) interaction is ignored. Subsequent inclusion of the *s-o* interaction the configurations determined by the central field and the residual electrostatic terms into a series of states characterised by the quantum numbers **L**, **S** and **J**, with **J** given by

$$\mathbf{J} = \sum_i \mathbf{l}_i + \sum_i \mathbf{s}_i = \mathbf{L} + \mathbf{S} \quad (9.3)$$

summing over all electrons. l_i and s_i are the orbital angular momenta and spins of the individual electrons respectively. The ground state of the configuration can be determined using Hund's rules which states that **S** and **L** are a maximum (subject to the Pauli exclusion principle). The ground state quantum numbers for holmium are **L**=6, **S**=2 and **J**=8. The *s-o* interaction, although smaller than the central field and the residual electrostatic interactions, is fairly large for the rare earths as a result of the high atomic number of the series. Thus there is a significant energy gap between the first excited state and the ground state. Therefore at room temperature only the ground state is appreciably populated, and so it is only necessary to consider the ground state when including additional perturbations.

In each rare earth atom there are two or three electrons in 6s and 5d shells outside a partially filled 4f shell and a xenon core. In the metallic state the outer electrons become delocalised to form a "sea" of conduction electrons around the tripositive metal ions, and the 4f shell remains largely intact, thus the magnetic properties of the ions closely resemble

those of the free atoms. The $4f$ shells of most rare earth elements possess a magnetic moment, and in the ground state the moments are ordered. In this state the $4f$ electrons are subjected to different interactions with their surroundings. These can be classified into two categories, firstly the single site interactions for which the interactions act at only one site, so that their influence on a $4f$ electron is unaffected by the magnetic state of its neighbours. The Hamiltonian from these interactions sums over atomic sites, i , but does not include any coupling between sites. The second category is the two-site interactions which are dependent on the magnetic state of the neighbouring ions, so that the $4f$ electron clouds are coupled between pairs of ions, giving terms involving i and j .

9.1.1.1 The crystal field

The crystal field interaction is the dominant single-site interaction. The charge distribution of the neighbouring atoms gives rise to a potential at an atom site, which can interact with the $4f$ electrons. The potential arising from ions sitting at positions $\mathbf{R}$ and the electrons at positions $\mathbf{r}$ has the form

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{R})d\mathbf{R}}{|\mathbf{r} - \mathbf{R}|} \quad (9.4)$$

where $\rho(\mathbf{R})$ is the charge distribution of the nuclei and electrons of the neighbouring atoms. If this does not penetrate the $4f$ charge cloud it can be regarded as a solution of Laplace's equation, and therefore the potential can be expanded around an ion-site in terms of spherical harmonics, $Y_{lm}(\mathbf{r})$ as explained by Jensen and Mackintosh [1]. However for the purpose of this work a rigorous theoretical treatment of the crystal field is less important than understanding the effect that the crystal field has. The expansion shows that it is the sign and relative magnitude of the crystal field parameters that strongly influence the energetically favourable orientations along which ordered magnetic moments will lie. The

crystal field essentially removes the spatial degeneracy of the angular momentum terms, because the electrostatic field set up by neighbouring charges is not isotropic.

9.1.1.2 Indirect exchange interaction

The most important two-site interaction in rare earth metals is the indirect exchange interaction. Because the $4f$ electrons are highly localised at the atoms there is virtually no overlap of adjacent charge clouds, and so the exchange cannot be direct but must be mediated by the conduction electrons, and is thus indirect (when charge clouds overlap there is a Coulomb interaction between the two electrons which is dependent on the symmetry and spin state). This indirect exchange is described by the Ruderman-Kittel-Kasuya-Yosida, RKKY model, developed to describe the complex nature of the interactions.

The RKKY model assumes a short-range exchange between the $4f$ electrons and the conduction electrons. The direct exchange Hamiltonian is written as

$$H_{sf} = -\sum_i \mathcal{I}(r - R_i) \mathbf{S}_i \cdot \mathbf{s}(\mathbf{r}) \quad (9.5)$$

where $\mathbf{S}_i$ is the $4f$ electrons spin at a site $\mathbf{R}_i$, $\mathbf{s}(\mathbf{r})$ is the conduction electron spin density at position $\mathbf{r}$, and $\mathcal{I}$ is the exchange integral which is determined by the overlapping of the $4f$ and conduction electrons charge cloud. This overlap causes the conduction band to be polarised and this polarisation is communicated throughout the metal. Therefore in the neighbourhood of another metal ion the conduction electron interacts with the $4f$ electrons leading to an effective $4f-4f$ interaction, which may be written in terms of the total angular momentum

$$H_{ff} = -\frac{1}{2} \sum_{i \neq j} \mathcal{J}(\mathbf{R}_i - \mathbf{R}_j) \mathbf{J}(\mathbf{R}_i) \cdot \mathbf{J}(\mathbf{R}_j). \quad (9.6)$$

The exchange function, $\mathcal{J}(\mathbf{R}_i - \mathbf{R}_j)$, is proportional to the conduction-electron susceptibility, or essentially the response of the conduction electrons to the exchange field of the localised $4f$ electrons. $\mathcal{J}(\mathbf{R}_i - \mathbf{R}_j)$ is a long-ranged function, with the inclusion of up to 8 nearest

neighbours necessary for some rare earth systems to describe the spin wave dispersion fully. The indirect exchange interaction is essentially the change in polarisation of the conduction electron by the spin of one ion, and the influence of this polarisation on the spin of a second ion.

The exchange constant is a function of the conduction electron susceptibility, which is essentially a measure of how easily an electron is able to respond to the polarising effects of a neighbouring atom. Many conduction electrons in a metal are not able to change their spin state because all the orbitals below the Fermi surface, which is a surface of constant energy in k -space which separates filled and unfilled orbitals, are already occupied. The Pauli exclusion principle, which states that no two electrons in a system can be in the same quantum state, means that electrons cannot just change their spin state, but that this is dependent on there being available orbitals with similar energy which they can occupy. By considering the detailed nature of the Fermi surface of a system [1], it can be seen that where pairs of states do exist that are separated by $\mathbf{q}$, of which one is empty and the other full, with both lying close to the Fermi surface, then these electrons are more able to respond easily. If the Fermi surface has flat, parallel (nested) regions then there exist many such pair states and there will be a peak in the susceptibility at the wavevector $\mathbf{q}$ which separates them.

9.1.1.3 Magnetoelastic effects

All the terms in the Hamiltonian considered so far have been appropriate for an unstrained lattice. However growth of single-crystal thin films of rare earth metals (and hydrides) can lead to appreciable strain in the systems because of the clamping of the α -lattice parameters. The interaction between the magnetisation and strain in the lattice is accounted for in the magnetoelastic energy term, and this can often be considerable.

9.1.2 Magnetism of rare earth hydrides

In the rare earth hydrides, the decrease in conduction electron density results in the magnetic manifestations that are dependent on the RKKY interaction being generally diminished. The changes in crystal structure for RH_2 and RH_3 , and the concomitant changes in the Fermi surfaces, fundamentally change the indirect exchange interaction through $\chi(\mathbf{q})$. Furthermore, away from stoichiometry the ordering into sublattices at low temperatures, as discussed in the previous chapter, can also change the magnetic properties dramatically. The excess hydrogen (deuterium) atoms in the β -phase of RH_{2+x} occupy the octahedral sites within the unit cell and changes the magnetic and transport properties of the system because the presence of the hydrogen modifies the local site symmetry. For example a rare earth atom site within the unit cell with all neighbouring octahedral sites vacant has a very different symmetry from the case when one octahedral site is occupied by hydrogen. Thus the crystal field and magnetic properties of the dihydrides can be expected to change as the $[\text{H}]/[\text{R}]$ ratio varies, as observed in, for example $\beta\text{-TbH}_{2+x}$ [6], $\beta\text{-DyH}_{2+x}$ [7] and $\beta\text{-ErH}_{2+x}$ [5]. Therefore a knowledge of the exact hydrogen (deuterium) concentration in a system is vital for correct interpretation of experimental data between systems.

Shaked *et al.* [2] determined the magnetic structure of the pure dideuteride HoD_2 , using neutron diffraction on powder samples. They found a commensurate antiferromagnetic, AF, structure described by a wavevector $\frac{1}{4}(113)\mathbf{A}$ (with $\mathbf{A} = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$ as defined in equation 4.3) below an ordering temperature of 4.5K. The moment direction was found to be $[8\bar{6}3]$ the closest symmetry direction being $[\bar{1}10]$. The spin function for the structure may be expressed [2] as

$$\mu(\mathbf{r}) = \sqrt{2}\hat{\mu} \cos\left(\frac{2\pi}{4}(r_x + r_y + 3r_z) + \frac{\pi}{4}\right) \quad (9.7)$$

where r_x , r_y and r_z are the relative coordinates in the unit cell and the direction of the spin axis determines the relative intensities of the magnetic Bragg reflections. Above this

temperature they found an incommensurate structure with a wavevector slightly different from $\frac{1}{4}(113)\mathbf{A}$ and a Néel temperature of 6K.

The neutron diffraction experiments by Vajda *et al.* on the $\beta\text{-HoH(D)}_{2+x}$ [3] system report an incommensurate AF structure for $\text{HoD}_{2.0}$ below the Néel temperature (6.3K). This structure is present at all temperatures down to 1.5K and coexists with a commensurate AF configuration, modulation vector $\underline{\mathbf{k}}=\frac{1}{4}(113)\mathbf{A}$, below a temperature T_1 ($\sim 3\text{-}4\text{K}$). $\underline{\mathbf{k}}$ defines the orientation along which the moments are modulated and in the case of a simple antiferromagnet, the modulation direction is defined by the modulation direction as shown in Figure 9.1. In the case of an antiferromagnetic structure with modulation vector $\underline{\mathbf{k}}=\frac{1}{4}(113)\mathbf{A}$ the magnetic unit cell is therefore equivalent to a $4 \times 4 \times 4$ array of chemical unit cells.

The moment in the commensurate phase is reported as $[4.63, \overline{2.67}, \overline{2.14}]\mu_B$, significantly different from the direction reported by Shaked. Very little work has been done on the magnetic structure of the superstoichiometric system, but Vajda *et al.* [3] report for

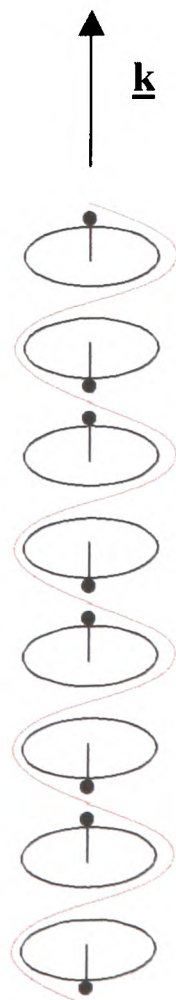


Figure 9.1: Schematic diagram of modulation vector for a simple antiferromagnet

HoD_{2+x} with $x=0.12$, a different magnetic structure to that of the stoichiometric dihydride with short range magnetic order below $T=8\text{K}$.

The magnetism in the stoichiometric phase appears to be similar for different rare earth systems. For example, the stoichiometric $\beta\text{-RD}_{2+x}$ ($R=\text{Tb}$ [6], Dy [11], Ho) systems adopt a sinusoidally modulated AF configuration with $\underline{k} = (\zeta, \zeta, 1-\zeta)\mathbf{A}$ with $\zeta=1/4$ for low T structures. The higher temperature AF structures with an incommensurate modulation vector appear to be different for the different rare earth systems. In $R=\text{Dy}$ [11] and Ho [3] the modulation vector is close to $(\zeta, \zeta, 1-\zeta)\mathbf{A}$ while for $R=\text{Tb}$ it is $(\zeta, \zeta, 1-2\zeta)\mathbf{A}$ [6]. The magnetism in the superstoichiometric phase also varies greatly between rare earth metals, for example in $\text{TbD}_{2.18,2.24}$ there is both a commensurate $\underline{k}_1 \sim (\zeta, \zeta, 1)\mathbf{A}$, and an incommensurate structure $\underline{k}_2 \sim (\zeta_1, \zeta_2, 1)\mathbf{A}$ whereas for $\text{DyD}_{2.135}$ and $\text{HoD}_{2.12}$ only short range ordering is observed.

9.2 Sample growth and characterisation

9.2.1 Sample growth

It is important to emphasize that all previous work on the magnetic structure of the HoD_{2+x} system has been carried out on bulk powder samples. In contrast we have used single-crystal samples to study the magnetic structures. Single crystal Ho layers were grown with the Balzers UMS630 MBE facility at Oxford. Sapphire substrates with an epitaxially polished $(1\bar{1}20) \pm 0.5^\circ$ surface were solvent cleaned and annealed under UHV at approximately 750°C in the growth chamber immediately prior to deposition. Two samples of 6 nm Nb/ 500 nm Ho / 5 nm Nb were deposited with a growth rate of 0.05nm/s . The Nb acts as a chemical buffer between the Ho and the sapphire, and as a capping layer to prevent

oxidation in air. The growth temperatures were 750°C for the Nb buffer, 500°C for the Ho film and room temperature for the Nb capping layer. Since deuterium is preferable to hydrogen for neutron diffraction studies because the scattering length of deuterium is larger and the incoherent cross-section is much smaller, subsequently one film was loaded with deuterium to the stoichiometric dideuteride state. The loading was achieved using a standard four-probe lock-in based technique to measure the resistivity in-situ to determine the degree of loading, in a UHV-based H reactor at KTH, Stockholm. The second sample was loaded with deuterium until it was in the superstoichiometric phase, with $x=0.21$.

9.2.2 X-ray diffraction

The films were initially studied by x-ray diffraction using a triple-axis diffractometer with a rotating anode source. The measurements confirmed that the samples were of single crystal form with the [111] direction perpendicular to the plane of the films. The room-temperature lattice constant of the nominally stoichiometric sample was measured as $a(\text{HoD}_2)=0.5153(2)\text{nm}$, and this is in agreement with the values obtained by Pebler and Wallace [12] of 0.5165 nm, indicating that the sample is the stoichiometric dideuteride. The 0.001 nm difference corresponds to the isotope effect observed in other systems [10]. An estimate of the deuterium concentration of the superstoichiometric dideuteride was made from the lattice constant, assuming a linear contraction of the lattice as a result of the increasingly ionic attractive interaction between the octahedral deuterium, using the lattice contraction β as measured by Vajda [3], where β is given by

$$\beta_{300K} = \left(\frac{1}{a} \right) \frac{\Delta a}{\Delta x} = -0.85(10) \times 10^{-2} / \text{atom D} . \quad (9.8)$$

The room-temperature lattice constant was measured as $a(\text{HoD}_{2+x})=0.5146 \text{ nm}$, and using equation (9.8) we can estimate the deuterium concentration to be $x=0.21 \pm 0.05$. There are no published values for the range of concentrations over which the pure dideuteride exists,

however by comparison with the range of existence of the pure dihydride ($-0.15 \leq x \leq 0.17$) it can be seen that this estimate is very close to the limit of the pure dideuteride range. However no trideuteride was detected in the scans, although an epitaxial oxide, with lattice constant $a(\text{Ho}_2\text{O}_3)=1.0630(2)$ nm was observed as a minority phase in both samples.

The x-ray measurements also showed that both fcc β -phase structural domains were present in similar proportions. Scans perpendicular and parallel to the growth direction revealed no significant differences in lattice parameter (± 0.0005 nm), showing that the structures are cubic within error, and that the films had fully relaxed to their bulk structure. This is because the thickness of the HoD_{2+x} films was far in excess of the critical thickness. The mosaic spreads of the samples were 0.66° . The mosaic spreads of the best thin films are typically 0.1° – 0.2° [13,14], but this is consistent with previous work on hydrides by the authors [15] and confirms that the crystalline quality of single crystal films is degraded during the $\alpha \rightarrow \beta$ transformation

9.2.3 Neutron scattering

The magnetic structure of the films was determined using neutron scattering experiments with the triple-axis spectrometer TAS1 at the DR3 reactor of the Risø laboratory, Denmark. The experiments measured the elastic scattering only, so as to reduce the background scattering. Neutrons from a cold source were Bragg reflected from the (002) planes of a pyrolytic graphite monochromator to produce a monochromatic neutron beam with a wavelength of 0.405 nm. The neutrons with wavelengths $\lambda/2$, $\lambda/3$, etc. were suppressed by a cooled Be filter. The samples were mounted in a variable temperature cryostat with the $[\bar{1}10]$ fcc direction normal to the plane of scattering, and so that (hhl) type wavevectors were accessible in the scattering plane. Temperatures between 1.5K and 300K

could be obtained and the temperature controlled to 0.1K. Most of the measurements were performed by radially scanning the wave-vector, transfer keeping the energy transfer fixed at zero. Particular emphasis was put on the (111) and $(\bar{1}\bar{1}0)$ structural Bragg reflections and the magnetic reflections for holmium dideuteride which can be considered as satellites of the fcc chemical lattice formed by the modulation vectors $1/4(113)\mathbf{A}$ and $1/4(\bar{1}\bar{1}3)\mathbf{A}$. Single-crystal measurements allow more direct determination of moment directions and ordering wave vectors than powder methods.

9.4 Results

In view of the conflicting results of Vajda and Shaked the samples were examined carefully, looking for the existence of both commensurate and incommensurate phases. From the results of Vajda and Shaked the system is known to order along a $1/4(113)\mathbf{A}$ type direction. In a single crystal sample oriented with the (hhl) plane as the scattering plane there are now 12 distinct $\langle 113 \rangle$ directions. Three directions are equivalent to the $1/4(113)\mathbf{A}$ modulation direction, three directions equivalent to the $1/4[\bar{1}\bar{1}3]$ modulation direction and there are six others which are inaccessible. Figure 9.2 shows a (111) stereographic projection of the fcc structure. The (hhl) scattering plane projects on to the horizontal diameter in the figure, and is indicated by the arrow in the figure. From the figure it can easily be seen that of the twelve possible ordering directions only two are accessible in this plane. This means that such experiments are only able to sample two of the three types of magnetic domains, and are not sufficient in themselves to be able to draw definitive

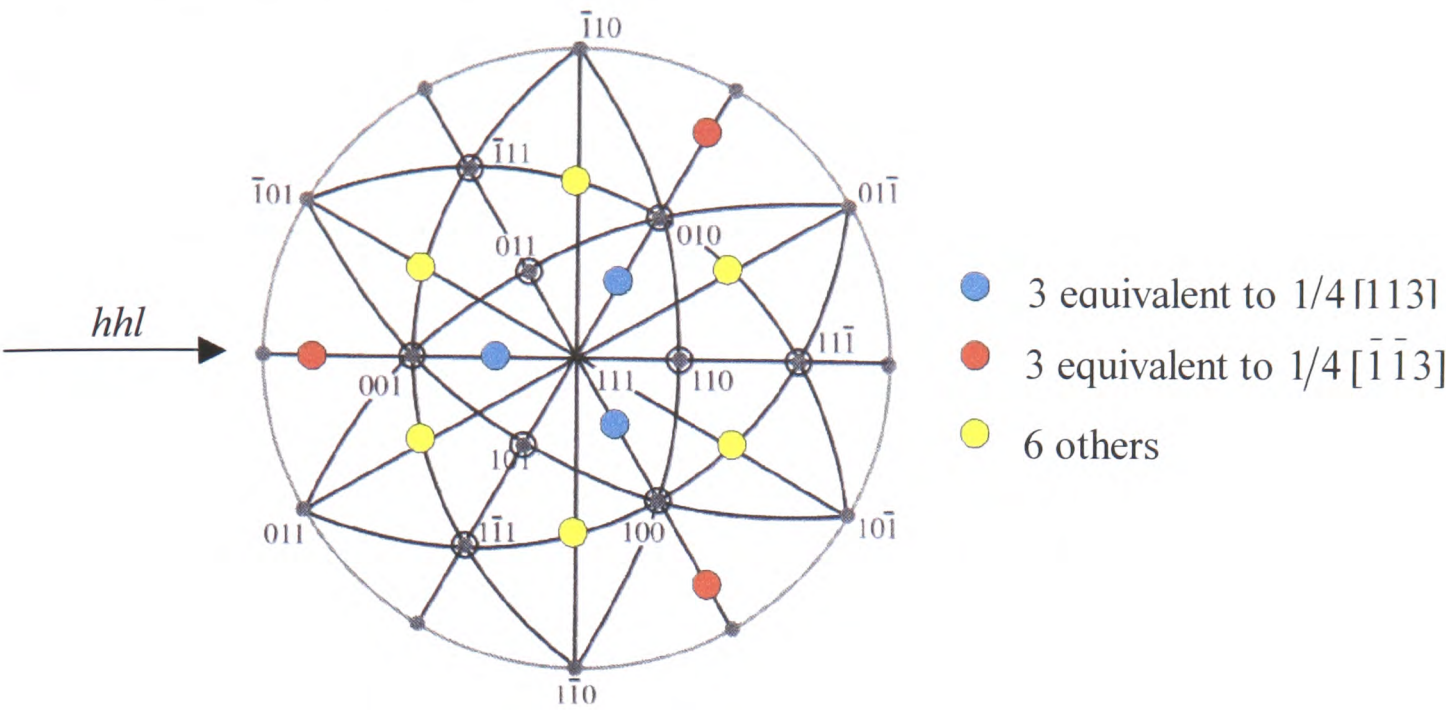


Figure 9.2: (111) stereographic projection to show the 12 equivalent $\langle 113 \rangle$ directions

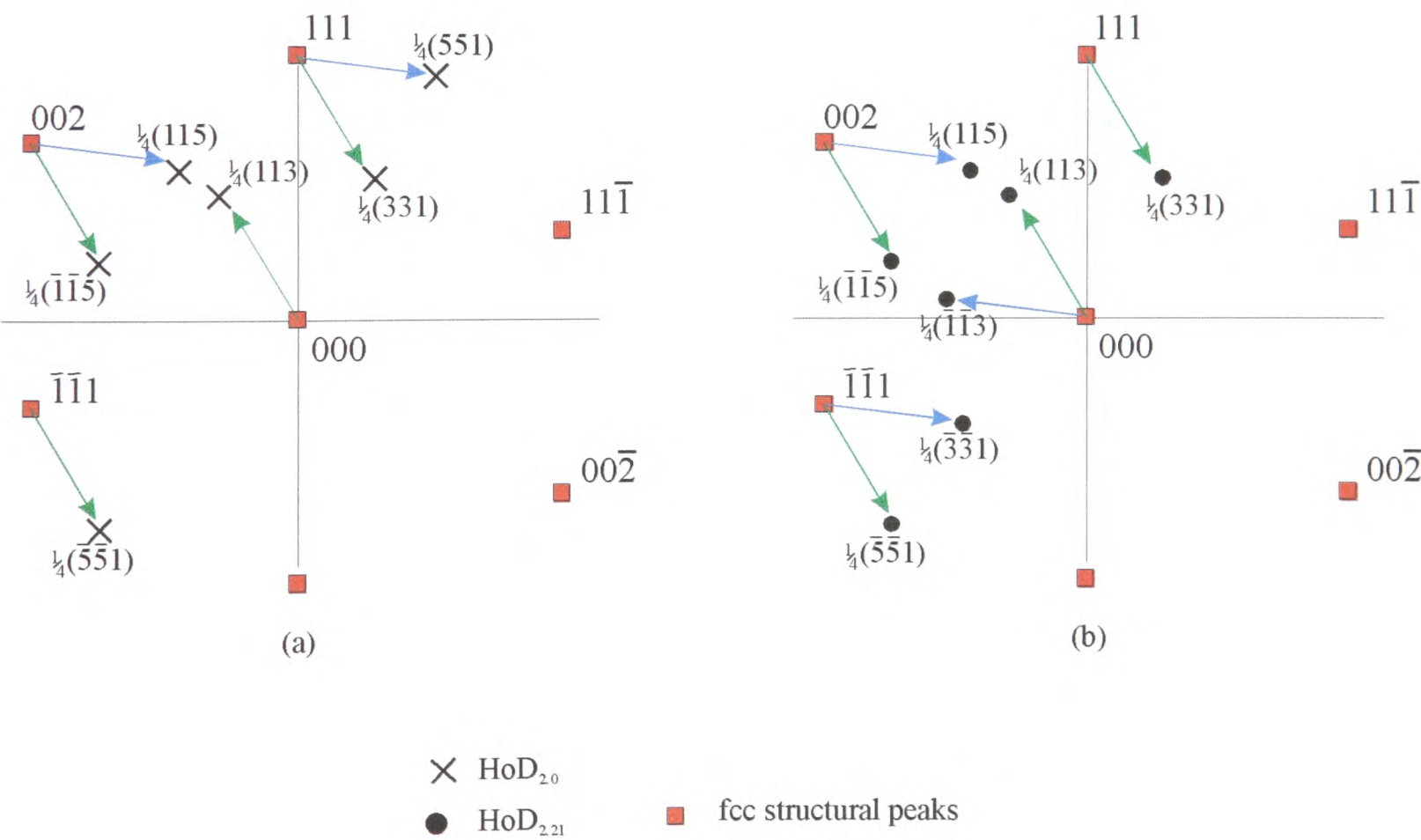


Figure 9.3: (a) the reflections observed for the stoichiometric $\text{HoD}_{2.0}$ sample (b) the reflections observed for the superstoichiometric $\text{HoD}_{2.21}$ sample. The figure shows that only one structural domain, but two magnetic domains (domain modulated along $\frac{1}{4}[113]$ - green arrows, domain modulated along $\frac{1}{4}[\bar{1}\bar{1}\bar{3}]$ - blue arrows), were examined.

conclusions as to how the domains, or specific modulation directions within the domains, are populated.

9.4.1 $\text{HoD}_{2.0}$

The wavevectors of the reflections observed for the $\text{HoD}_{2.0}$ sample are shown in Figure 9.3(a). Six magnetic peaks were studied in total. The Néel temperature of the system was measured as $T_N=4.1\pm0.4$ K, and the plot of peak intensity versus temperature from which this ordering temperature was determined is shown in Figure 9.4. The incommensurate phase has a modulation vector $(\frac{1}{4}+\delta_1, \frac{1}{4}+\delta_1, \frac{3}{4}+\delta_3)\mathbf{A}$ with $\delta_1=0.029(2)$ and $\delta_3=-0.006(2)$. The intensity observed when the wavevector was varied radially along (331) is shown in Figure 9.5(a) for a temperature of 1.5K. The structure was found to have two magnetic domains, modulated along the $\frac{1}{4}(113)\mathbf{A}$ and $\frac{1}{4}(\bar{1}\bar{1}3)\mathbf{A}$ as shown in Figure 9.5(a). Each domain contained both an incommensurate and a commensurate structure. From the theory outlined in section 4.5, a program was written to calculate how the intensity of the magnetic peaks varied with moment direction. From comparison of the calculated and measured intensities of the incommensurate peaks in each domain it was possible to determine the moment direction. It was not possible to perform the same calculation on the intensities observed from the commensurate phase as in the majority of radial scans the incommensurate phase dominates, however from the limited data available from the commensurate phase the peak intensities appeared to be in similar ratio to the peak intensities of the incommensurate phase, implying similar moment directions. Figure 9.6 shows the measured intensities (black circles) with the calculated fit. The red triangles

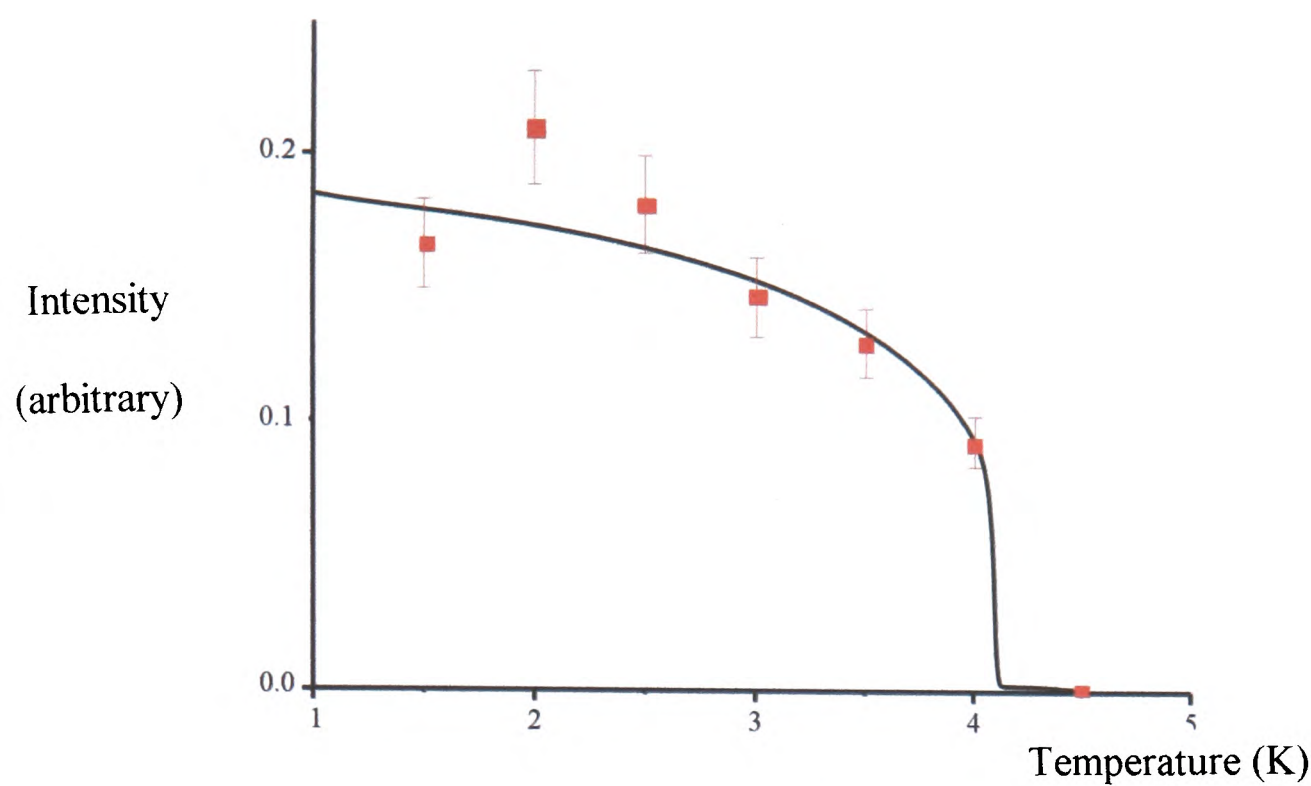


Figure 9.4: Graph of Intensity v. Temperature for $\text{HoD}_{2.0}$ sample

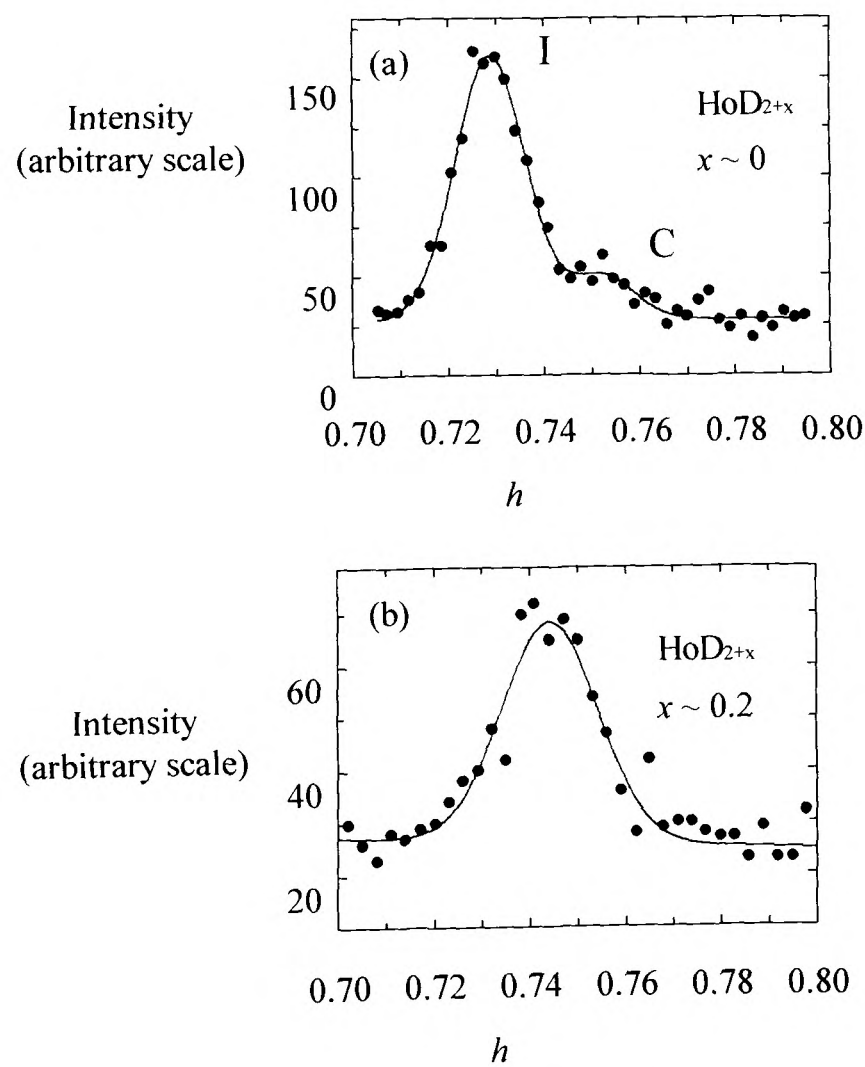


Figure 9.5: scans across the $(\frac{3}{4} \frac{3}{4} \frac{1}{4})$ magnetic peak of HoD_{2+x} in the $[hhl]$ radial direction for (a) $x=0$ showing the presence of incommensurate (I) and commensurate (C) wavevectors, and (b) for $x=0.21$ showing presence only of a commensurate peak

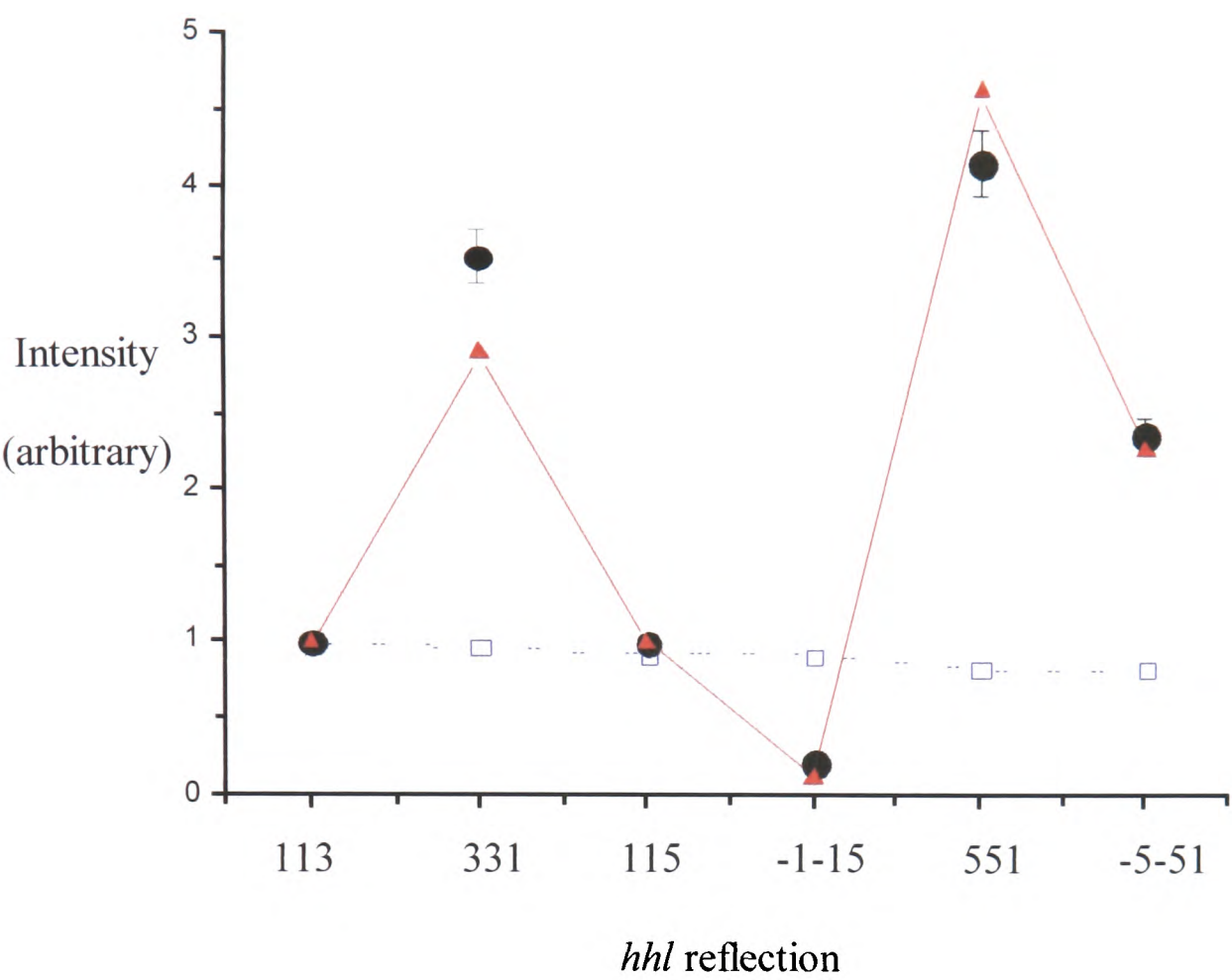


Figure 9.6: Plot of the magnetic intensity for $\text{HoD}_{2.0}$ film showing the measured intensity (black circles) with the calculated intensity for a moment direction close to $[001]$ shown with red triangles, and for a moment direction close to $[\bar{1}\bar{1}0]$ (as predicted with previous powder measurements) as blue squares.

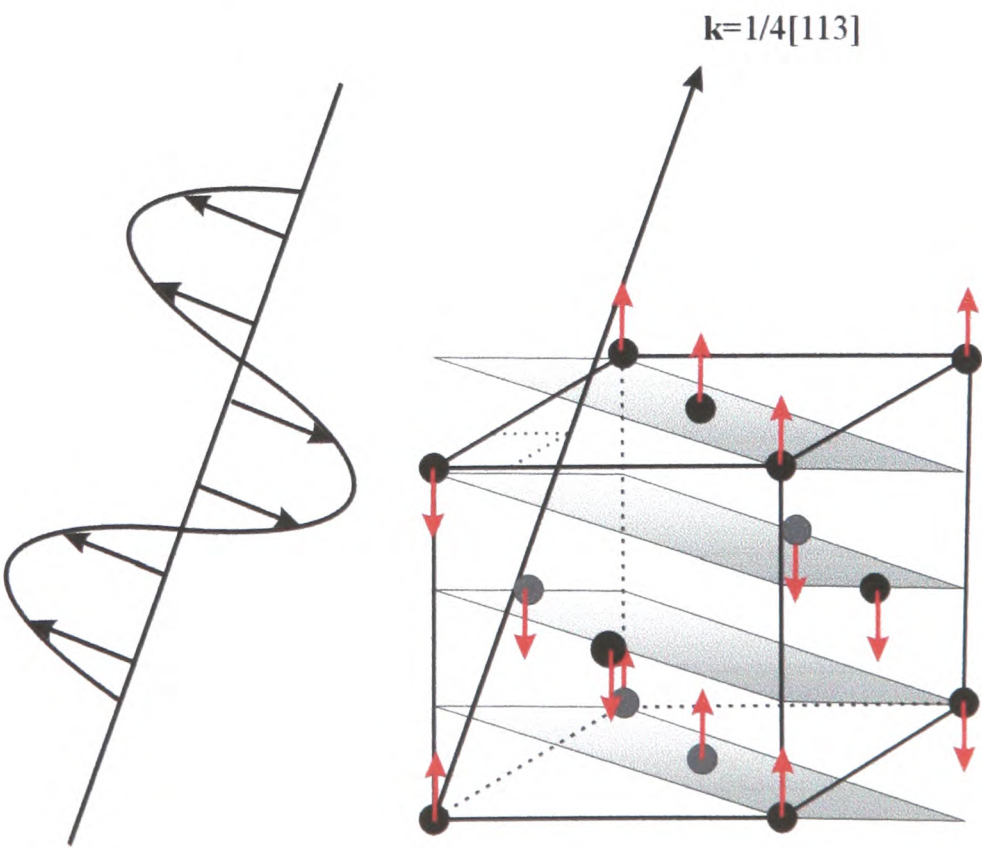


Figure 9.7: Proposed magnetic structure and projection of the moments upon the direction of the propagation vector in stoichiometric $\text{HoD}_{2.0}$

show the best achievable fit to the data which is consistent with the moments lying along $[0, -0.2, 0.9]$ i.e. close to the $[001]$ direction. The blue squares show the calculation for the moments lying along $[\bar{1}10]$ as previously reported by Shaked *et al.* From the quality of the fit in both domains it can be seen also that both magnetic domains are approximately equally populated, which is expected because the absence of strain within the lattice gives no reason to expect preferential domain population. Figure 9.7 shows a schematic diagram of the proposed spin structure for stoichiometric $\text{HoD}_{2.0}$.

9.4.2 $\text{HoD}_{2.21}$

The addition of deuterium interstitials has a dramatic effect on the magnetic ordering for $\text{HoD}_{2.21}$. The observed reflections for $\text{HoD}_{2.21}$ are shown in Figure 9.3(b). Eight magnetic peaks were studied. The structure was observed to consist of only an incommensurate antiferromagnet, again exhibiting two magnetic domains, with modulation vectors close to $\frac{1}{4}(113)\mathbf{A}$ and $\frac{1}{4}(\bar{1}\bar{1}3)\mathbf{A}$. The incommensurate phase has a modulation vector $(\frac{1}{4}+\delta_1, \frac{1}{4}+\delta_1, \frac{3}{4}+\delta_3)\mathbf{A}$ with $\delta_1=0.002(2)$ and $\delta_3=-0.004(2)$. The incommensurate transition temperature was $4.5\pm0.1\text{K}$, and the plot of intensity versus temperature is shown in Figure 9.8.

Figure 9.5(b) shows the scan along (331) for this sample. The two samples ($\text{HoD}_{2.0}$ and $\text{HoD}_{2.21}$) have identical structural widths in the radial scans and mosaic spread but the magnetic peaks in Figure 9.5 are significantly broader than the structural peaks, and furthermore there appears to be a reduction in correlation length at the higher stoichiometry from 53 nm in the stoichiometric $\text{HoD}_{2.0}$ to 40 nm in the superstoichiometric sample. The moments of the incommensurate structure are found to lie close to the $[3\bar{3}\bar{1}]$ direction in the $\frac{1}{4}(113)\mathbf{A}$ modulated domain, and close to $(\bar{3}\bar{3}\bar{1})\mathbf{A}$ for the $\frac{1}{4}(\bar{1}\bar{1}3)\mathbf{A}$

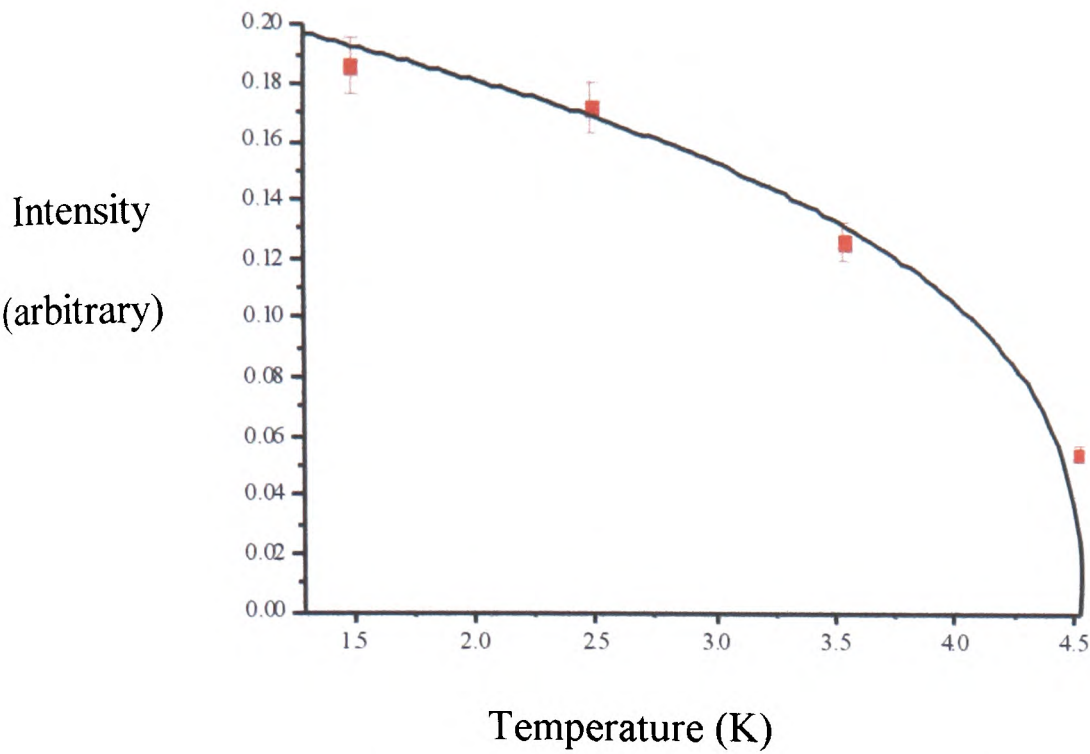


Figure 9.8: Graph of Intensity v. Temperature for $\text{HoD}_{2.21}$ sample

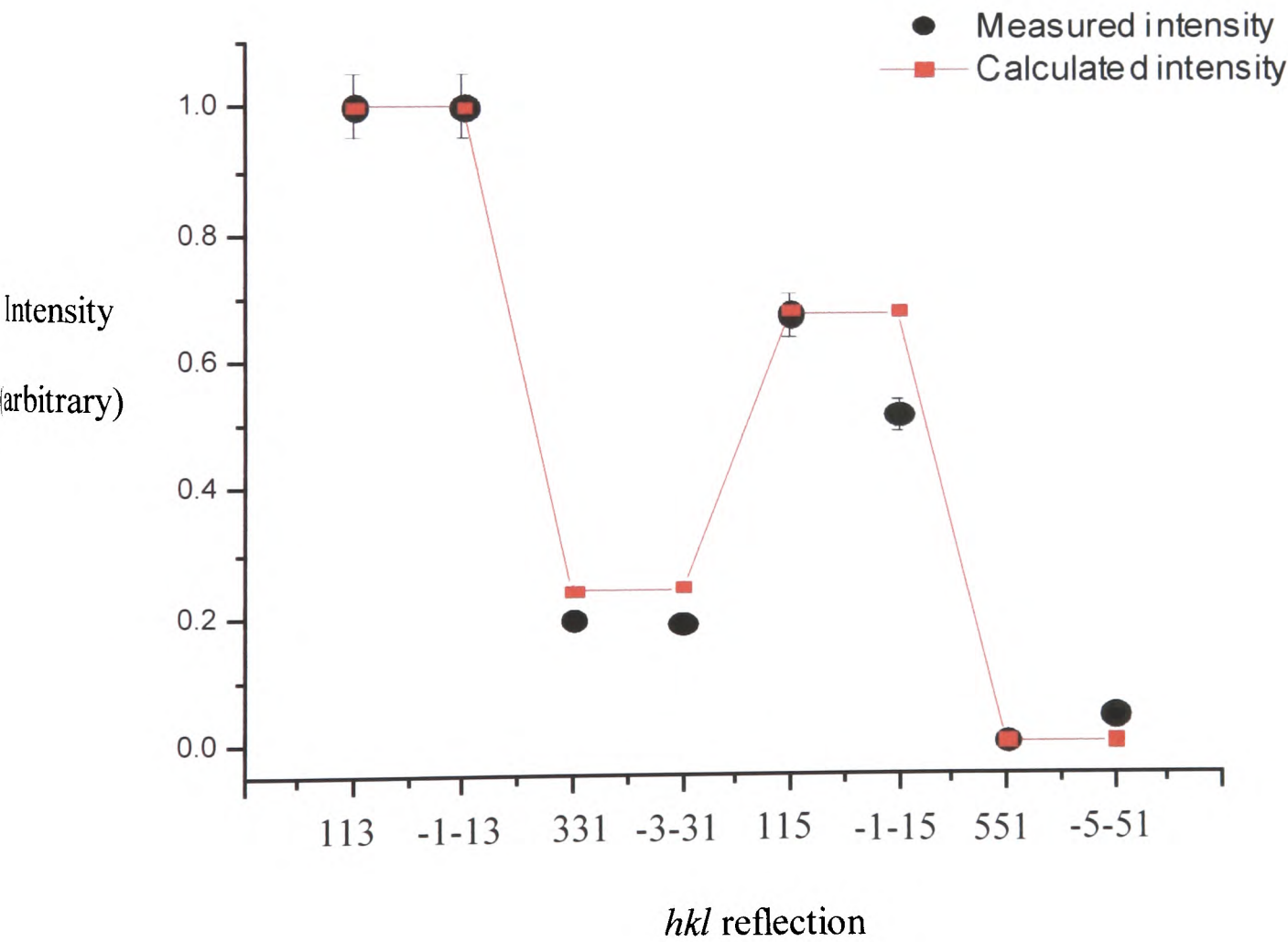


Figure 9.9: Plot of the magnetic structure factor for $\text{HoD}_{2.21}$ film showing measured intensity (black circles) and calculated intensity (red squares) . Moment direction is along $[3\bar{3}1]$ for the domain modulated along $\frac{1}{4}[113]$ and $[\bar{3}\bar{3}1]$ for the domain modulated along $\frac{1}{4}[\bar{1}\bar{1}3]$

modulated domain and the results of the analysis are shown in Figure 9.9. A diagram of the proposed spin structure is shown in Figure 9.10.

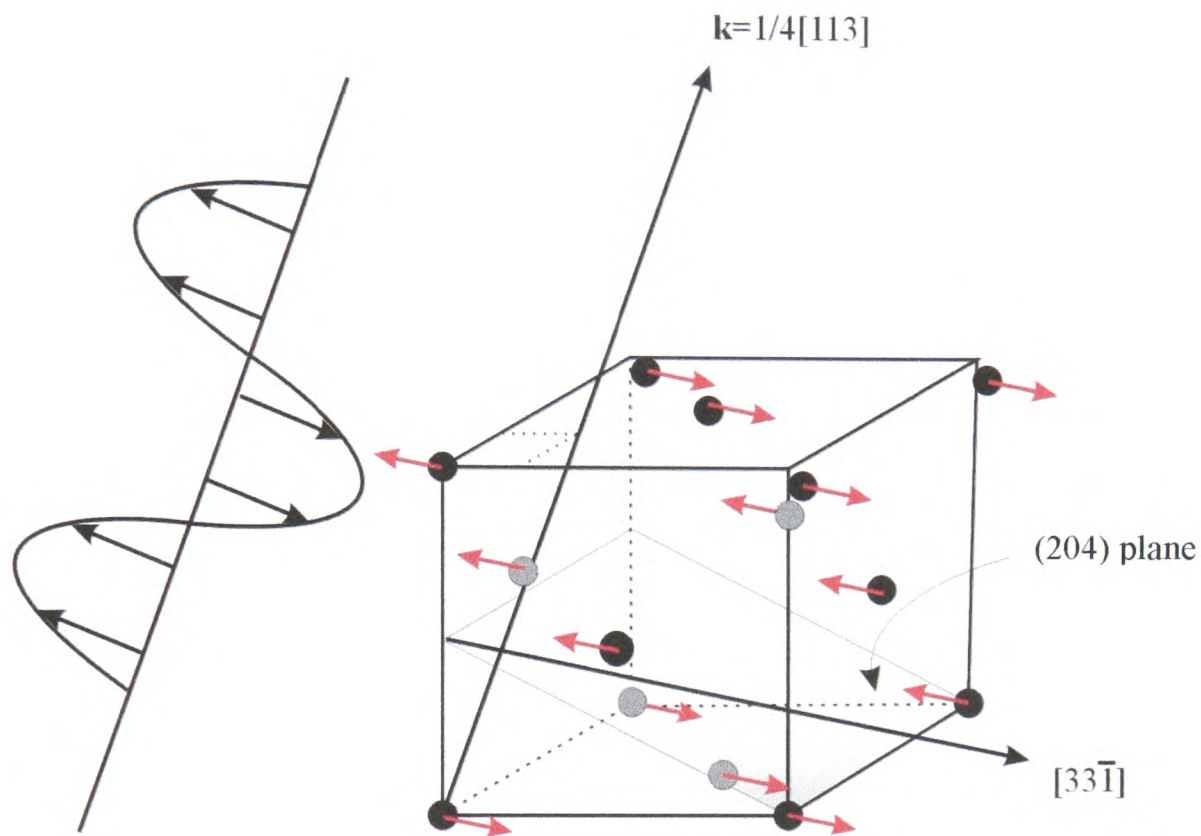


Figure 9.10: Proposed magnetic structure and projection of the moments upon the direction of the propagation vector in superstoichiometric $\text{HoD}_{2.21}$

9.5 Discussion

The observation of the two magnetic phases in the stoichiometric sample, and the observed modulation direction, agrees with the results of Vajda *et al.* However, the observed ordering temperature of $T_N = 4.1 \pm 0.4 \text{ K}$ is lower than their published result of 6.3 K, and is closer to the ordering temperature observed by Shaked *et al.* of 4.5 K for the commensurate structure. The incommensurate structure observed in the $\text{HoD}_{2.21}$ sample was not reported by Vajda *et al.* The moment direction determined in the single-crystal experiments was quite different to either of the moment directions reported previously.

The average moment per Ho site was calculated from the single crystal data. However the results were unphysical suggesting that it is incorrect to assume a random population of domains. Both Vajda *et al.* and Shaked *et al.* calculated the moment in $\text{HoD}_{2.0}$ from neutron measurements on powder samples; the latter found a magnetic moment of $6.4(4)\mu_B$ and the former $5.76(0.03)\mu_B$. The magnetic moment gJ , where g is the gyromagnetic ratio and J the total angular momentum, on a Ho^{3+} ion in the metallic state is $10\mu_B$. Thus we can see that despite the discrepancy between the two moment values in the literature, the magnetic moment of the metal ions in $\text{HoD}_{2.0}$ is significantly reduced from that of the metal ions in the metallic state and hence it is apparent that the crystal field is dominant, and determines the ground state of the crystal.

The ordering wavevectors are determined by the interaction between the moments. The most important two-site interaction in rare earth metals is the indirect exchange interaction. Simple considerations with an isotropic exchange constant do not yield the periodicities observed in the rare earth hydride systems. Therefore it is necessary to consider the form of this interaction in more depth. As already discussed the exchange constant is a function of the conduction electron susceptibility, and parallel (or nested) regions of the Fermi surface will have many such pair states and will produce peaks in the susceptibility. Liu considered the Fermi surface of RH_2 and found three types of possible nesting. The configuration that nested the largest area, and hence contained the maximum number of electron pair states occurred for the wavevector $(\zeta, \zeta, 1-\zeta)$ which is exactly satisfied by the deuterides of Tb, Dy and Ho with $\zeta=0.25$. However none of the nesting configurations were able to predict the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ ordering observed in GdH_2 [9] and this fact suggests that more than one interaction may be important. R A Cowley (*private communication*) has considered the effect on the stable ordering wavevectors of including the dipole-dipole interaction.

Although the ordering in HoD_{2+x} can be explained without the inclusion of the dipole-dipole interaction, the necessity of its inclusion to explain the ordering observed in other rare earth systems implies that it may also be important in this system. For two ions i and j the classical dipole-dipole interaction is of the form

$$H_{dd} = -\frac{1}{2} \sum_{ij} D_{\alpha\beta}(ij) \mathbf{J}_{i\alpha} \cdot \mathbf{J}_{j\beta} \quad (9.9)$$

where $D_{\alpha\beta}(ij)$ is the strength of the dipole-dipole coupling. This interaction is typically one or two orders of magnitude less than the exchange between nearest neighbours, but can have a significant effect on the magnetic structure due to the highly anisotropic and extremely long-ranged nature of the interaction, as has been observed in the low temperature structures of Ho.

Preliminary calculations by Cowley including the dipole-dipole interaction at discrete points have predicted that the magnetic structure could order along the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})\mathbf{A}$ and $(0.9 \ 0.9 \ 0.3)\mathbf{A}$ modulation wavevector under certain circumstances. With more detailed calculations it is hoped to prove the stability of the $(\frac{3}{4} \ \frac{1}{4} \ \frac{1}{4})\mathbf{A}$ ordering wavevector. The possible importance of $D_{\alpha\beta}(ij)$ for Ho is supported by the broadening of the magnetic peaks particularly in the superstoichiometric sample. Short range order was also observed by Vajda *et al.* in $\text{HoD}_{2.12}$. The presence of a short-range magnetically ordered structure indicates that there is competition between more than one interaction.

The spin structures of the two films, as shown in Figures 9.7 and 9.10, are clearly different because of the change of symmetry of the two crystal structures. The previous measurements on HoD_2 by Shaked *et al.* propose a moment direction close to $[\bar{1}10]$ however, experiments on the single-crystal thin films reveal a moment direction close to $[001]$. TbD_{2+x} has also been observed to order in a direction parallel to $[001]$ for low deuterium concentrations [2]. However, in addition to the different spin directions, there are

other significant differences in the structures observed. The single-crystal results show both an incommensurate and a commensurate phase whereas the powder studies of Shaked report only a commensurate phase, and the powder studies of Vajda report the presence of both commensurate and incommensurate phases. The data used to determine the spin direction were obtained from the incommensurate phase, as this peak dominates most hhl radial scans, however from the limited data available, the commensurate phase peak intensities appeared to be in a similar ratio to the peak intensities of the incommensurate phase, implying similar moment directions. From measurements on the two samples, $\text{HoD}_{2.0}$ and $\text{HoD}_{2.21}$, it can be deduced that the magnetic ordering is very sensitive to stoichiometry and it could be that a comparison between the two sets of work is invalid because the deuterium concentration differed between the single-crystal and powder samples.

From the symmetry of the fcc fluorite system, the only symmetry operation that leaves the ordering wavevector $\mathbf{q} = (\frac{1}{4} \frac{1}{4} \frac{3}{4})\mathbf{A}$ invariant is the mirror plane between x and y . The moment directions are subject to the same symmetry conditions as the wavevector, and therefore must also be invariant under the same symmetry operation. There are therefore only two types of moment direction possible, $[a \ -a \ 0]$ or $[a \ a \ b]$. These directions do not agree with the observed moment orientation of Shaked ($[8\bar{6}3]$) or Vajda ($[4.63, \overline{2.67}, \overline{2.14}]$), but are consistent with a moment direction of $[001]$ proposed by the current research work.

The cubic symmetry is broken for $\text{HoD}_{2.21}$ and it is interesting to consider the differences in magnetic structure in terms of the deuterium sublattices. It is known that in the concentration range $0.12 \leq x \leq 0.25$ in TbD_{2+x} , the excess deuterium atoms order with the DO_{22} structure [16] in which every fourth $\{420\}$ plane is filled, with the intermediate 3 planes remaining empty. There are indications from both resistivity and lattice constant measurements [3] that a similar ordering occurs in HoD_{2+x} although neutron diffraction work by Vajda et al was unable to detect any structure attributable to a DO_{22} superlattice.

The intensity of the peaks that would result from such an ordering would not have been detectable in the thin film samples studied in this chapter. However, the moment direction observed for the superstoichiometric phase could be another indication towards such ordering. The $[3\bar{3}1]$ direction lies only 6° out of the (204) plane, as shown in Figure 9.10, and so it appears that the moments are now trying to order in the planes in which the octahedral deuterium atoms are lying.

9.6 Conclusions

The use of MBE grown Ho films loaded with deuterium to form HoD_{2+x} enables single-crystal magnetic neutron diffraction techniques to be employed; a technique that allows a more direct determination of moment directions and magnetic modulation wavevectors than can be attained on powder samples. The assignment of the moment direction for $x=0.0$ disagrees with powder measurements on HoD_2 , but in contrast agrees with the $[001]$ direction found previously for TbD_2 . The $x=0.21$ sample has a different magnetic structure to the stoichiometric sample. The result suggests that the excess deuterium forms the superlattice structure observed in TbD_{2+x} .

References

- [1] J. Jensen and A. R. Mackintosh *Rare earth Magnetism: Structures and Excitations*, Oxford University Press, New York, (1991).
- [2] H. Shaked, D. G. Westlake, J. Faber, and M. H. Mueller, *Phys. Rev. B* **30**, 328 (1984).
- [3] P. Vajda, G. Andre, and O. J. Zogal, *Phys. Rev. B* **57**, 5830 (1998).
- [4] P. Vajda and J. N. Daou, *Z. Phys. Chem.* **179**, 443 (1993).

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- [5] P. Vajda and J. N. Daou, *Phys. Rev. B* **49**, 3275 (1994).
- [6] P. Vajda, J. N. Daou, and G. Andre, *Phys. Rev. B* **48**, 6116 (1993).
- [7] P. Vajda and J. N. Daou, *Phys. Rev. B* **45**, 9749 (1992).
- [8] A. Boukraa, P. Vajda, and J. N. Daou, *Z. Phys. Chem.* **179**, 453 (1993).
- [9] S. Hémon, R. A. Cowley, R. C. C. Ward, M. R. Wells, L. Douysset, and H. Ronnow, *J. Phys. C* **12**, 5011 (2000).
- [10] P. Vajda "Hydrogen in rare-earth metals, including RH_{2+x} phases", in *Handbook on the physics and chemistry of rare earths*, Vol. 20, edited by K. A. Gschneidner Jr. and L. Eyring, Elsevier Science, 208 (1995).
- [11] P. Vajda, G. Andre, and J. Hammann, *Phys. Rev. B* **55**, 3028 (1997).
- [12] A. Pebler and W. E. Wallace, *J. Phys. Chem.* **66**, 148 (1962).
- [13] D. Jehan, D. F. McMorrow, R. A. Cowley, R. C. C. Ward, M. R. Wells, N. Hagmann, and K. N. Clausen, *Phys. Rev. B* **48**, 5594 (1993).
- [14] R. A. Cowley, R. C. C. Ward, M. R. Wells, M. Matsuda, and B. Sternlieb, *J. Phys. C* **6**, 2985 (1994).
- [15] E. J. Grier, O. V. Kolosov, A. K. Petford-Long, R. C. C. Ward, M. R. Wells, and B. Hjörvarsson, *J. Phys. D.: Appl. Phys.* **33**, 894 (2000).
- [16] G. Andre, O. Blaschko, W. Schwarz, J. N. Daou, and P. Vajda, *Phys. Rev. B* **46**, 8644 (1992).

Chapter 10

Conclusions and further work

To conclude, a summary is given of the main results from the microstructural characterisation of epitaxial rare earth metal based films, and possible further work is discussed. The aim of this work was to characterise, at an atomic scale, the structure of rare earth metal thin films and superlattices, applying the technique of high resolution electron microscopy, HREM, to these systems for the first time.

All the epitaxial rare earth systems considered for this research project were grown on the (110) Nb on $(11\bar{2}0)$ sapphire substrate system. As the quality of the niobium layer influences how well the rest of the structure will grow the initial work concentrated on characterising the substrate system. In-situ reflection high energy electron diffraction, RHEED, experiments showed that for molecular beam epitaxy, MBE, growth with the substrate temperature held at 750°C and a Nb growth rate of 0.05 nm/s, then initially the Nb is deposited with hexagonal symmetry, attributed as being an NbO fcc phase due to Nb bonding with the oxygen termination layer of the Al_2O_3 substrate. After the deposition of approximately 2 monolayers the layer relaxes to the bulk bcc Nb structure and the Nb proceeds to grow monolayer by monolayer for approximately the first 20 planes of bcc growth.

Complementary use of HREM and conventional transmission electron microscopy, CTEM, uniquely identified the dislocation network for the semicoherent

$(110)_{\text{Nb}} \parallel (11\bar{2}0)_{\text{Al}_2\text{O}_3}$ interface to consist of pure edge dislocations, with the Burgers vectors parallel to the interface plane. The Burgers vectors of the dislocations are $\underline{\mathbf{b}} = \frac{1}{2}[\bar{1}11]$ and $\underline{\mathbf{b}} = \frac{1}{2}[\bar{1}\bar{1}1]$, with line directions $\frac{1}{3}[\bar{1}1\bar{2}]$ and $\frac{1}{3}[\bar{1}12]$ respectively. As these correspond to the Burgers vectors characteristic of bulk niobium, it implies that the misfit dislocations do not alter the atomic structure of the coherent regions. This work has shown that it is possible to use the combination of CTEM and HREM techniques for the unique identification of misfit dislocation networks at a niobium/sapphire interface, but for this research the techniques have only been applied to the $(110)_{\text{Nb}} \parallel (11\bar{2}0)_{\text{Al}_2\text{O}_3}$ interface because of our allied interest in epitaxial rare earth systems. As there exists a three dimensional orientation relationship between niobium and sapphire, further work could be undertaken in the unique characterisation of the misfit dislocation network for different niobium/sapphire interfaces.

TEM specimen preparation techniques applicable for the rare earth metal systems were developed. Conventional specimen preparation techniques, including broad ion beam milling, were found to produce specimens that were significantly changed from the initial film, and the specimens were found to consist of the dihydride and oxide, frequently leaving no trace of the initial α -phase metal structure. The dihydride is thought to form during the specimen preparation process by the reaction of the metal with water or residual hydrogen within the broad ion beam milling chamber. The reaction with water vapour is made more likely by the necessity of cooling a specimen during milling to liquid nitrogen temperature during thinning to prevent mixing of the layers, as the water vapour will condense on the specimen surface upon cooling. However, it was possible to prepare α -phase metal specimens using a focused ion beam system, but the reaction of the rare earths with water or residual hydrogen remained a problem. It was found that specimens of thickness greater

than ~25 nm remain in the α -phase metal structure, but for thinner specimens ($< 20\text{nm}$) it is observed that the dihydride forms throughout the specimen thickness leaving no trace of the metal. In specimens of intermediate thicknesses ($\sim 20\text{ nm}$) it is observed that the hydrogen does not populate both the Ho and Y layers equally, but that the Y layers are in the β -phase whilst the Ho layers remain in the α -phase. In general it is observed that Ho is in the α -phase for specimens of thickness as small as 21nm whereas α -phase Y is not observed in specimens thinner than 26nm. Specimens thinner than 21 (26) nm are completely changed to the β -phase for Ho and Y respectively. Preliminary work (*private communication* – Wiebke Löhstroh) on the hydrogen loading of Ho/Y superlattices with in-situ XRD also observes the Y layers forming the β -phase before the Ho layers. The reasons as to why Y preferentially forms the β -phase over Ho are unclear, and further work into the mechanisms of hydrogenation and why one layer preferentially absorbs hydrogen is clearly desirable so that the structural and chemical properties of the systems can be further explained.

HREM was also used to characterise a Ho/Y superlattice. The superlattice consisted of 40 monolayers of Ho with 20 monolayers of Y, and this bilayer was repeated 30 times. Both the Ho and Y layers were thicker than the critical thickness for this system (calculated as 14.5 and 15 monolayers for Ho on Y and Y on Ho respectively). Misfit dislocations were identified at the Ho/Y interfaces as having a partial Burgers vector of $\underline{b} = \frac{1}{3}[0\bar{1}10] + \frac{1}{3}[0\bar{1}10]$ is not a lattice vector of the crystal, but is a partial dislocation which forms after the dissociation of the Burgers vector $\underline{b} = \frac{1}{3}\langle 11\bar{2}0 \rangle$ into two partials on the (0001) slip plane. It was calculated that for thicknesses just above the critical thickness the strain present within the system will be of order $\sim 1.3\%$. Therefore the changes in lattice parameters of the layers due to the partial relief of strain are not measurable by electron diffraction

techniques, where the errors in the measurement are at best $\sim 2\%$. However it was possible to conclude that the strain was not fully relieved, as for full relaxation of the strain in the layers a misfit dislocation would be needed every 50 planes. This was not observed and so there is residual strain present within the system. Previous work with X-ray and neutron diffraction concludes that such systems remain coherently strained for individual layer thicknesses much greater than researched for this work. The possibility of the interfaces being semicoherent and the system left with a residual strain, as identified in this research, does not seem to have been considered. It is possible that the interfaces identified with X-ray and neutron diffraction techniques as being coherent were in fact semicoherent and hence further work combining the techniques of HREM with X-ray and neutron diffraction could be used to investigate in detail the strain relief mechanisms and the effect of such strain relief on the magnetic and other properties of the systems.

Further work is needed in the area of TEM specimen preparation techniques. Preparing samples under UHV conditions should essentially remove the possibility of the rare earth metal films reacting with water or residual hydrogen and should enable the preparation of thinner α -phase metal specimens. Thinner specimens would enable the use of additional characterisation techniques, for example electron energy loss spectroscopy, and would improve the contrast in HREM images (which is reduced in images of thicker specimens due to multiple scattering events). The preparation of samples under UHV would also enable a more complete determination of the strain relief mechanisms within rare earth superlattices. Further work into the strain present within the Ho/Y superlattice characterised as part of this research was excluded because of the reaction of the film with hydrogen during specimen preparation. As in general TEM specimens do not have parallel sides, but are wedge shaped, a typical specimen of the superlattice exhibited thin areas of α -Ho - β -YH₂ layers, slightly thicker areas showing resolvable crossed lattice planes with both

layers being in the α -phase and much thicker areas showing unresolvable lattice planes. Thus the specimens were not wholly representative of the bulk film, and it was not possible to use such specimens for more detailed work on the strain relaxation mechanisms. Preparation of samples where the $\alpha \rightarrow \beta$ phase transformation is inhibited would therefore be of great value. Samples prepared such that the electron beam can be aligned along the $[1\bar{1}00]$ sapphire direction (i.e. orthogonal to the specimens in this research) would also enable the determination of the dislocation network.

The extreme reactivity of the rare earths as encountered in TEM sample preparation initiated investigations into other crystallographic rare earth compounds. The identification of the presence of the dihydride, RH_2 , and in certain cases the sesquioxide, R_2O_3 led to these structures being studied in their own right, in addition to the recent resurgence in interest in rare earth hydride thin films because of their remarkable ability to absorb up to three hydrogen atoms per rare earth atom. The absorption of hydrogen leads to a range of interesting physical properties, for example during hydrogen loading there is a continuous decrease in the carrier density, which gives rise to a metal-insulator transition in the interval between RH_2 and RH_3 . It is known that metallic 'mirror-like' films become transparent upon hydrogen loading between RH_2 and RH_3 and that the loading is reversible. Specimens of epitaxial thin films of RH_2 ($R=Ho, Y$) were studied with HREM and the crystallographic structure was confirmed as being face-centred cubic with the orientation relationship of the β -phase relative to the α -phase being $(0001)_{\alpha-phase} \parallel (111)_{\beta-phase}$, with $[2\bar{1}\bar{1}0]_{\alpha-phase} \parallel [\bar{1}10]_{\beta-phase}$. It was inferred from the presence of Moiré fringes in the images of the dihydride (spacing 0.746 ± 0.013 nm, lying at $\sim 35^\circ$ to the growth plane) that there was an epitaxial oxide on the surface of the dihydride.

Several studies on the hydrogen loading of thin films have shown that the single crystal nature of the films is preserved throughout the cycling between the α (metal), β (dihydride) and γ (trihydride) phases, accommodating the changes of structure of the rare earth metal lattice (hcp (α) - fcc (β) - hcp (γ)). However there are conflicting reports about the extent of the deterioration in crystalline perfection which occurs as a result of the loading/unloading cycles. Atomic force microscopy, AFM, ultrasonic force microscopy, UFM, and controlled environment transmission electron microscopy, CETEM, were employed to study in more detail the structural changes which occur during hydrogen loading of thin epitaxial films of holmium. The AFM and UFM analysis revealed that macroscopic features (ridges) form in a triangular pattern on the surface, aligned along the $\langle 110 \rangle$ type directions, as defined relative to the β -phase film. The ridge formation is attributed to the precipitation of the β - and γ -phases in turn within the host lattices, the α - and β -phases respectively. In each case the lattice of the precipitating phase is significantly expanded with respect to the host lattice (8.7% and 10.5% respectively at the two phase changes in the Ho-H system). There is an additional constraint on the accommodation of this expansion because of epitaxial clamping in the plane of the sample. As a result it is likely that the initial nucleation and growth of the precipitating phase will take place along inclined slip planes of the host lattice, leading to material being forced out of the surface in ridges which denote the edges of the precipitating plates. Therefore the ridges are aligned along the intersections of inclined slip planes with the surface plane. In the CETEM analysis it was observed that in the β -phase twin boundaries were confined to the (111) twin planes parallel to the substrate. After loading with hydrogen to superstoichiometric HoH_{2+x} (i.e. $x > 0$) twin boundaries were observed out of the plane as well. Associated with the latter twin boundaries is a characteristic image contrast in which every third plane appears in sharp contrast and the two layers in between have a lower contrast. Both these

observations indicate that slip occurs in the superstoichiometric β -phase prior to precipitation of the γ -phase. Such slip may provide precipitate nucleation sites for the ridge formation. There remain, however, discrepancies between this research and that of other groups. Kerssemakers *et al.* also find that such ridges form in YH_2 films on CaF_2 substrates, but that the ridges form only at the α - β phase transition and that the ridge network remains unchanged through further cyclic (un)loading between YH_2 and YH_3 . Because the work of the two groups employed different rare earth metal films (i.e. this research used Ho and Kerssemakers *et al.* used Y) and different substrate systems (sapphire and CaF_2 respectively) further work using similar substrate systems and rare earth layers would be of great interest to investigate the different observations of the two groups.

Because of the presence of unidentified phases present in the diffraction patterns from conventionally prepared TEM specimens, an investigation was undertaken into the ability of electron diffraction techniques to detect hydrogen within a heavy metal lattice, as one possible explanation of the unidentified structures was the ordering of the excess hydrogen present in the β - RH_{2+x} phase. In fact the simulated diffraction patterns ruled out the presence of ordered hydrogen superlattices within the specimens studied, but opened up the possibility of using electron diffraction as a viable alternative to neutron diffraction for studies of hydrogen ordering and indeed showed that it may be a preferable choice of technique in cases of limited sample volume, for example epitaxial thin films. Further work should include the preparation of specimens with a range of hydrogen concentrations within the β -phase, and then characterisation of the hydrogen sublattices could be undertaken with HREM. Preparing samples so that diffraction patterns can be taken along a combination of zone axes would enable a determination of the symmetry and therefore also the possible structure.

The final part of this research considered the effect that hydrogen (deuterium) superlattice structures have on the magnetic properties of MBE-grown Ho films loaded with deuterium to form HoD_{2+x} . Single-crystal magnetic neutron diffraction studies were carried out on these systems for the first time and this allowed a more specific determination of magnetic moment and magnetic modulation wavevector than previous work which used powder samples. The ordering wavevectors were determined for both samples to be along $\frac{1}{4}(113)\text{\AA}$ and $\frac{1}{4}(\bar{1}\bar{1}3)\text{\AA}$. Simple considerations with an isotropic exchange constant do not yield such ordering wavevectors and therefore it is necessary to consider this and other interactions in more depth. Preliminary calculations by R. A. Cowley (*private communication*) including the dipole-dipole interaction at discrete points have predicted that the magnetic structure could order along the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})\text{\AA}$ and $(0.9 \ 0.9 \ 0.3)\text{\AA}$ modulation wavevector under certain circumstances. More detailed calculations are needed to hopefully prove the stability of the $(\frac{3}{4} \ \frac{1}{4} \ \frac{1}{4})\text{\AA}$ ordering wavevector. The assignment of the moment direction to be close to $[001]$ for $\text{HoD}_{2.0}$ disagreed with previous powder measurements on HoD_2 , but such magnetic ordering has been observed previously in the TbD_2 system. The $\text{HoD}_{2.21}$ sample had a different magnetic structure to the stoichiometric sample, with the moments appearing to align in the $\{420\}$ type planes. The only rare earth system in which a deuterium superlattice has been directly observed is the TbD_{2+x} system, and in this system it was found that every fourth $\{420\}$ plane was filled with deuterium, with the intervening three planes empty. Thus the change in the symmetry of the system due to the ordering of excess deuterium atoms on the octahedral sites within the fcc lattice is seen to affect the magnetic properties of the system.

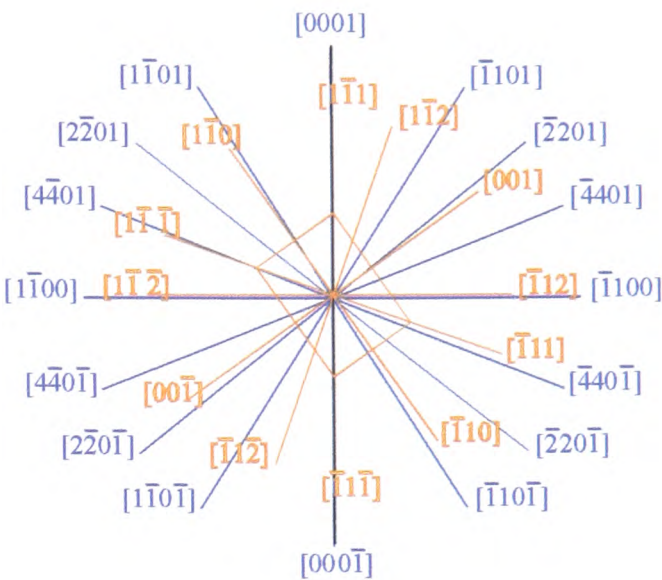
There is considerable scope for further experimental work on the magnetism of rare earth hydride systems. In particular, for the superstoichiometric range of the β -phase very little known about how the magnetic properties change as a function of hydrogen

(deuterium) concentration. The two samples considered as part of this research were at the extremes of the range of existence of the pure β -phase (although no data is available for the range of existence of the pure dideuteride, comparison with the range of existence of the pure dihydride $-0.15 \leq x \leq 0.17$ shows that a deuterium concentration of 2.21 must be near the mixed β - γ phase boundary). A detailed characterisation of the magnetic properties of a series of samples with a range of deuterium concentrations within the β -phase would be of great interest to investigate the effect of the extra deuterium atoms on the magnetic properties. For example, at present it is not known whether the moment direction changes gradually with the deuterium concentration, or whether there is an abrupt transition point. Using samples of increased volume may also enable direct correlation between the magnetic and chemical structure of the sample.

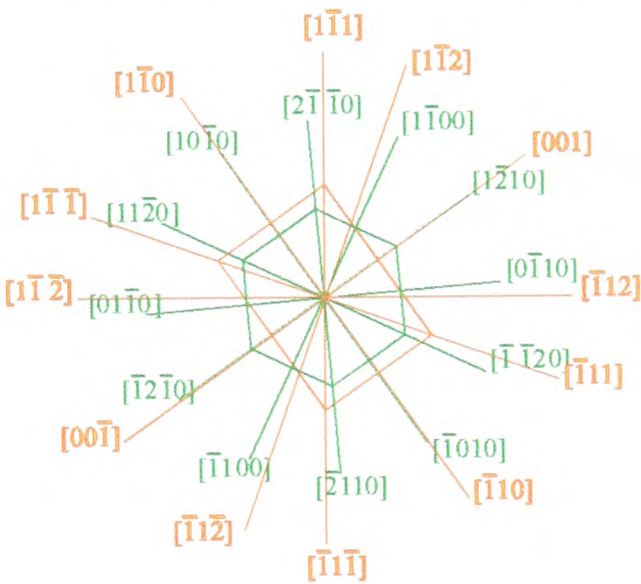
The study of the microstructure of rare earth films with HREM have to date been limited, and with the techniques developed within this thesis there is considerable scope for further experimental work on these systems.

Appendix 1: Orientation Relationships (OR) of epitaxial rare earth systems

OR between $(11\bar{2}0)$ $\alpha\text{-Al}_2\text{O}_3$ and (110) niobium



OR between (110) niobium and (0001) RE metal



OR between (0001) RE metal and (111) RH_2

