Rare-earth thin films and superlattices

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Abstract
This paper reviews neutron and x-ray diffraction studies of the magnetism of rare-earth thin films and superlattices grown using the LaMBE Facility in Oxford. Epitaxial strain is found to change the magnetic ordering and surface effects are shown to alter the critical exponents for phase transitions. The magnetic coherence across spacer layers is found to depend on the band structure of the superlattice as a whole, and the conduction-electron spin-density wave responsible for interlayer magnetic coupling is measured directly.

Keywords: rare earth, thin film, superlattice, magnetic structure, phase transition, interlayer coupling

(Some figures may appear in colour only in the online journal)

1. Introduction
The development of molecular beam epitaxy (MBE) has enabled new structures to be grown one atomic plane at a time on top of single-crystal substrates. Figure 1 shows some typical epitaxial structures. In the case of thin films, this means that entirely new structures can be stabilised that are not otherwise observed in nature. The magnetic properties of thin films are often quite different to bulk crystals. Critical exponents at phase transformations are different, and transitions are often suppressed, leading to very different magnetic structures. Physical behaviour in the solid state is dominated by the presence of the underlying crystal lattice, and the ability to introduce artificial periodicity in superlattices makes it possible to produce systems with tailor-made physical properties.

Bulk rare earths exhibit a very rich variety of antiferromagnetic structures, with the magnetic modulation mainly along the hexagonal *c* direction [1]. Depending on the exchange interaction and the single-ion anisotropy, for heavy rare earths this can lead to an incommensurate basal plane spiral, longitudinal modulation along *c*′, a commensurate cone phase with a ferromagnetic component along *c*″ and bunching of moments near to easy axes in the plane, a cycloidal phase, and for light rare earths antiferromagnetic coupling along *c*′ with multi-*q* modulation within the hexagonal plane. Exploring how these magnetic structures and their phase transformations change when combined with nonmagnetic spacer layers and each other in a superlattice is of great interest.

The magnetic interactions in bulk rare earths are well understood via the Ruderman–Kittel–Kasuya–Yosida (RKKY) model of indirect exchange [2–4]. The local 4f moments are coupled via the spin polarisation of the conduction electrons, and a peak in the conduction-electron susceptibility along *c*″ is responsible for the observed modulation. Rare-earth superlattices comprising successive blocks of magnetic material separated by blocks of nonmagnetic material have been shown to exhibit remarkable properties, the most notable being the coherence in the magnetic ordering between adjacent blocks [5]. Magnetic coupling has been observed across nonmagnetic spacer layers with thicknesses in excess of 100 Å. This is very surprising since measurements of the spin-wave dispersions of bulk rare earths indicate that the exchange extends to sixth-nearest neighbours only. Furthermore, the nonmagnetic block does not simply act as an inert spacer between the blocks of magnetic material. Instead it is found that there is a phase shift, proportional to the length of the nonmagnetic block, introduced between neighbouring magnetic blocks.

In this paper I shall review the contribution of Roger Cowley to our understanding of rare-earth thin films and superlattices. His previous breakthroughs in the
development of neutron and x-ray scattering techniques, and on the understanding of bulk rare-earth magnetism, phase transformations and magnetic exchange interactions gave him a unique perspective from which to approach this topic. I shall describe the main experimental techniques, focussing on MBE and triple-crystal diffractometers, and then I shall choose a subjective set of examples that illustrate his contributions to the understanding of the magnetic ordering, phase transitions and interactions in rare-earth films and superlattices.

2. Experimental techniques

All of the single-crystal thin films and superlattices were grown by MBE using the Balzers UMS 630 equipment in the LaMBE Facility at the University of Oxford, see figure 2 [6]. Elements were evaporated from either electron-beam sources or Knudsen effusion chambers in an attempt to obtain layer-by-layer growth. This was achieved by the choice of the growth temperature in relation to the melting point, where the compromise is to obtain sufficient surface diffusion to limit surface roughness, while minimising bulk inter-diffusion at the interfaces. The samples were grown on Y (001) seed layers (∼1800 Å) deposited onto a Nb buffer layer (∼1500 Å) on a sapphire substrate. In order to protect the magnetic structure from oxidation an yttrium capping layer was grown (∼250 Å).

The chemical structures were determined mainly using low- and high-resolution triple-crystal diffractometers on a rotating anode source in Oxford, see figure 3. The resolution function for triple-crystal x-ray diffraction determined by Roger Cowley is dominated by the monochromating and analysing crystals, and it depends on either the mosaic structure or, for perfect flat crystals, it is determined by the reflectivity, which is controlled by the Darwin width [7]. Expressions can be derived for the case when the source is a line spectrum (e.g. for a rotating anode) and when it has a continuous spectrum (e.g. for a synchrotron). Low resolution is employed to detect weak scattering from ultra-thin films or weak higher harmonic reflections, high resolution is required to determine accurate line shapes to measure correlation lengths.

The magnetic structures were determined by neutron diffraction, mainly using triple-axis spectrometers at Risø National Laboratory in Denmark, and also using a two-axis reflectometer at the National Institute of Standards and Technology in the United States. Energy analysis was employed to separate the weak magnetic diffraction from the ultra-thin films from the inelastic background from the much thicker substrates. Magnetic ordering was also investigated using resonant elastic x-ray scattering (REXS) at the European Synchrotron Radiation Facility in France and the National Synchrotron Light Source in the United States. At the synchrotrons triple-crystal diffractometers were again employed, and this time the analyser crystal was chosen to enable polarisation analysis of the scattered beam in order to separate the magnetic signal from the charge scattering background.

3. Results

3.1. Magnetic ordering in Ho thin films and Ho/Y superlattices

Bulk Ho orders below \( T_N \sim 132 \text{ K} \) in an incommensurate basal plane spiral, and bunching of moments about the in-plane easy directions leads to the formation of a commensurate cone structure below \( T \sim 18 \text{ K} \) [8–10]. High-resolution REXS studies led to the proposal of spin slip structures [9], and Roger Cowley’s careful neutron diffraction studies tied down these magnetic structures in terms of commensurate regions separated by spin discommensurations [10] and explained the thermal evolution and the effect on the ultrasonic elastic constants [11]. Neutron diffraction measurements of the magnetic structure of Ho films and Ho/Y superlattices by Roger Cowley show that epitaxial strain leads to very different magnetic ordering [12]. The temperature dependence of the average turn angle between successive planes is shown in figure 4, and in films and superlattices the value is always greater than for bulk. At low temperatures the cone phase is suppressed and instead the observation of high-order magnetic satellites indicate that the moments form long-period, commensurate spin-slip structures. The effective turn angle per layer in Y is the same for all samples, and independent of temperature. A comparison of the widths in the growth direction (parallel to the hexagonal c-direction) of the first and higher harmonics indicates that while the phase and coherence of the spiral is preserved across the Y blocks, there is no correlation in the positions of spin-slips in successive Ho blocks.

3.2. Magnetic phase transitions in Ho thin films

The phase transitions of thin films differ markedly from those of bulk crystals. Roger Cowley demonstrated that below the Néel temperature \( T_N \), the critical exponent \( \beta = 0.5 \) for films of elemental Ho and its alloys [13, 14], and this is inconsistent with the values reported for bulk Ho \((0.37–0.39)\) [15, 16]. A further puzzle arising from REXS measurements for bulk Ho is the observation of a second longer length scale [17]. Roger Cowley tackled these issues by growing a Ho film on a seed of an yttrium–lutetium alloy with a concentration chosen to provide lattice matching with the Ho layer [18]. The film was then capped by a thick alloy film of the same composition. The aim was to reduce epitaxial strain in the Ho film and to clamp it so that the magnetic film did not

Figure 1. Schematic diagram of some epitaxial structures: (a) sandwich, (b) superlattice, (c) basal-plane spirals separated by nonmagnetic layers.
Figure 2. The Balzers UMS 630 LaMBE growth equipment at Oxford.

Figure 3. Schematic diagram of a triple-crystal diffractometer in real space showing the directions of the nominal wave vectors, $k$, and the deviations, $\gamma$, of a typical ray [7]. Reproduced with permission from [7]. © International Union of Crystallography.

have a free surface, preventing magnetic fluctuations from coupling to elastic waves. The order parameters measured using neutron diffraction and REXS shown in figure 5 yield a critical exponent $\beta = 0.37(3)$ in agreement with the bulk value, and a dramatically suppressed second length scale component. The results confirm that the second length scale is associated with the crystallographic surface rather than the termination of the magnetic layer, and suggest that it is associated with the coupling between the order parameter and the free strains at the surface, the thick cap clamping the upper surface of the magnetic layer inhibiting its response to the order parameter fluctuations.

3.3. Competing anisotropies in Ho/Er superlattices

Bulk Er orders below $T_N \sim 84$ K in a longitudinal modulated structure with a similar modulation wave vector to Ho at the ordering temperatures, but the crystalline anisotropy favours moments along the hexagonal $c$-direction [19]. Between $T \sim 18–52$ K it forms a number of long-period commensurable modulated structures with components in the basal plane and along $c$ [20], and at low temperature it forms a cone structure. Roger Cowley discovered that the intermediate temperature structure in the bulk is based on an elliptical cycloid in the $a$–$c$ plane with an oscillating moment in the $b$-direction with a different period, and there is trigonal bunching of moments in the low-temperature cone phase [21]. He found that for Ho/Er superlattices at temperatures below $T_N$ for Ho and above that for Er, the Ho orders in a basal plane spiral and this order propagates through the paramagnetic Er so that there is coherence over many bilayer repeats, see figure 6 [22]. Below $T_N$ for Er the widths of the Ho peaks increase indicating a reduction in coherence, and an additional broad magnetic reflection is observed from the longitudinal Er order which is confined to individual Er blocks. The lack of coherence of the Er ordering cannot be understood in terms of the RKKY model that successfully explains magnetic coupling in bulk rare earths. Instead these results point towards the need for the matching of wave functions of conduction electrons at the interfaces in superlattices. The driving force for coherent long-range order is the decrease in the energy of the conduction electrons if they are no longer confined to a single block.

3.4. Conduction electron spin density waves in Nd/Pr superlattices

Neodymium orders below $T_N \sim 19.9$ K with an antiferromagnetic coupling between hexagonal layers and an incommensurate sinusoidal modulation in the basal plane [23]. As
the temperature is lowered a series of multi-\( q \) magnetic structures are observed [24, 25]. Praseodymium has a non-magnetic singlet ground state and does not exhibit long-range magnetic order until it is induced by the hyperfine interaction at \( T_N \sim 50 \) mK [26, 27]. Roger Cowley suggested studying interlayer magnetic coupling in Nd/Pr superlattices, where the incommensurate modulation is perpendicular in the basal plane [28].

This approach was extended in REXS measurements performed on Nd/Pr superlattices [29]. The species sensitivity of the technique enables the magnetism of different components of a superlattice to be studied separately. REXS at the L edges of rare earths is dominated by virtual electric dipole transitions from a 2p core level to the 5d bands and, therefore, it gives direct information of the conduction electron spin density waves. In this sense it gives complementary information
Figure 6. Magnetic scattering along (100) for Ho/Er superlattices showing (a) a coherent basal plane spiral for $T_{N}(Er) < T < T_{N}(Ho)$ and (b) additional magnetic scattering from Er confined to a single Er block for $T < T_{N}(Er)$ [22]. Reprinted figure with permission from [22], © 1994 American Physical Society.

Figure 7. REXS from a Nd/Pr superlattice [29]. (a) X-ray energy scans with $Q$ fixed at a magnetic Bragg peak showing the resonant enhancement at the Pr and Nd L_{II} edges. (b) Temperature dependence of scans in the $c$ direction through the magnetic Bragg reflections, showing magnetic superlattice peaks. (c) The amplitude of the magnetic polarisation of the 5d bands as a function of depth used to calculate the scattering in (b). Reproduced from [29]. © IOP Publishing Ltd. All rights reserved.

to neutron diffraction, which tends to be dominated by scattering from the ordered 4f moments. Furthermore, high intensity and narrow resolution enable the magnetic structures and their coherence through the superlattice to be studied more closely than before.

Figure 7 presents the scattering from Nd/Pr in scans of x-ray energy with wave vector fixed at a magnetic Bragg reflection close to the ordering wave vector of bulk Nd. The scattering was observed to resonate at the L_{II} edges of Pr and Nd, showing that the 5d bands are magnetically polarised in both elements. Scans of wave vector in the growth direction through the magnetic peaks at the Pr and Nd L_{II} edges give information on the propagation of magnetic order through the superlattice. The moment profile through the magnetic blocks determines the intensities of the magnetic superlattice peaks, and the broadening of the peaks at the higher temperatures shows a decrease in the coherence of the magnetism. The magnetic polarisation follows the concentration profile at all temperatures at the Nd resonance. The results show that an almost uniform moment is induced across the Pr block at low temperature, whereas the induced moment at the centre of the Pr block is very small at elevated temperature, where the coherence is reduced. The results demonstrate that the observed conduction-electron spin-density wave in Pr is responsible for the coupling between successive Nd blocks.

4. Discussion & conclusions

Other compositions of heavy rare-earth superlattice studied by Roger Cowley include Ho/Lu [30], where coupled ferromagnetic blocks are observed at low temperature, Ho/Sc [31] where the large lattice mismatch leads to a lack of coherence of the hexagonal stacking sequence in successive blocks and in turn to a decoupling of the magnetism, Ho/Tb [32] where coherent basal plane spirals coexist with
ferromagnetic structures, Ho/Tm [33] which resembles Ho/Er, and Er/Lu [34] where coherent c-axis modulated spin-density wave and cycloid structures were observed. In the case of light rare-earth superlattices, the growth of single-crystal Ce films and superlattices with different stacking sequences of hexagonal layers allowed their magnetic order to be explored [35], and the interplay between magnetism and superconductivity was investigated for antiferromagnetic Nd/La [36] and ferromagnetic Gd/La [37, 38] superlattices.

Roger Cowley’s studies of magnetic phase transitions in thin film samples have contributed significantly to our understanding. In particular, by growing Ho films between lattice-matched and clamping seed and capping layers, it is found that the critical exponents agree with bulk measurements, and the scattering associated with the second longer length scale is essentially eliminated. This result is of interest for a much wider range of materials, since the second length scale has been observed for many other bulk structural and magnetic phase transitions in rare earth metals and actinides, see reference [39] for a review by Roger Cowley. Dy/Lu superlattices have subsequently been used as model magnetic systems in which to study surface reconstructions in surface magnetic phase transitions [40].

Roger Cowley’s new understanding of the interlayer coupling mechanism in terms of the wave matching functions arising from the studies of Ho/Er superlattices has a wider significance. For example, coupling is observed in superlattices with ferromagnetic blocks separated by nonmagnetic spacer layers, including the rare-earth systems Ho/Lu [30] and Dy/Lu [41]. In these cases the coupling across the spacer layer is either ferromagnetic or antiferromagnetic rather than helical, as would be expected for induced spin density waves. These ideas readily extend to the technologically important transition-metal giant magnetoresistance systems, where coupling of ferromagnetic blocks across nonmagnetic spacer layers occurs in a similar manner [42, 43].

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