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Soft x-ray diffraction study of magnetic ordering in holmium

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Abstract

We have conducted the first single-crystal resonant soft x-ray diffraction study of the magnetic order in holmium at the Ho M_V edge. Both the $(0, 0, \tau)$ and $(0, 0, 2\tau)$ satellite reflections can be accessed at the M_V edge. Energy scans through these reflections display very different line shapes. The behaviour of the integrated intensity and wavevector modulation was similar to that observed in earlier neutron and resonant x-ray diffraction studies at the L edges, which showed that valid qualitative results can be obtained using the soft x-ray diffraction technique. The sample absorption at the M_V edge is considerable, reducing the penetration depth to approximately 100 Å.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The usual technique for magnetic structure determination is single-crystal neutron diffraction. On the other hand, x-rays can also observe the associated magnetic moment but the interaction is typically 10^8 times weaker than the dominant charge scattering. However, in 1972 de Bergevin and Brunel [1] reported the observation of very weak reflections associated with the magnetic order in the antiferromagnet NiO using a copper x-ray tube. The development of synchrotron sources meant that very intense photon fluxes became available, and this, combined with the tunability of the incident photon energy coupled with the high degree of polarization, led to a dramatic advancement in magnetic x-ray scattering. The magnetic structure in holmium was

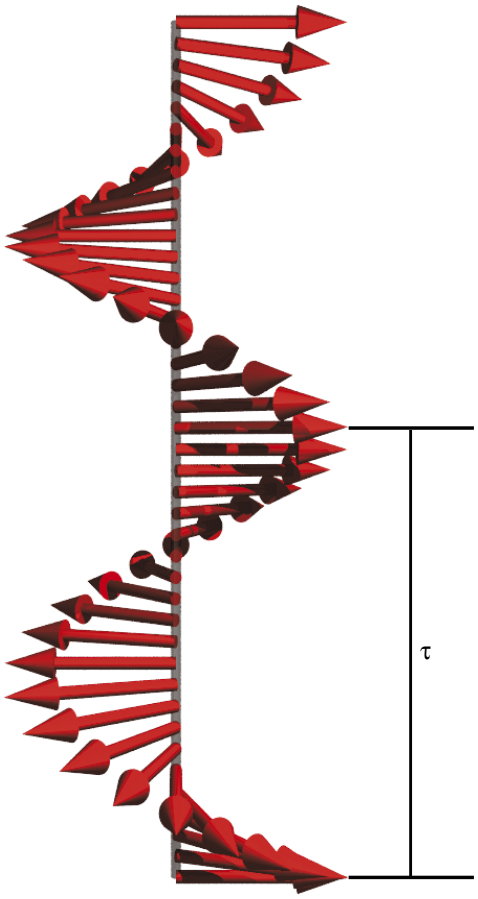

Figure 1. Schematic of helical magnetic order in holmium. The τ unit cell is outlined.

successfully studied with non-resonant x-ray scattering at a synchrotron source by Gibbs *et al* [2]. However, upon tuning the incoming x-ray photon energy to the Ho L_{III} absorption edge a large resonant enhancement of approximately 50-fold was observed [3].

Holmium crystallizes into a hexagonal close packed structure with lattice parameters $a = b = 3.57$ Å, and $c = 5.61$ Å. It has the outer shell configuration $4f^{10}$ with an $^5I_8$ ground state configuration. The magnetic moment per Ho atom is approximately 10 μ_B. The magnetic structure of holmium was first studied by Koehler *et al* [4, 5] using neutron diffraction. They observed a spiral magnetic structure below the Néel temperature of 133 K. In this structure the magnetic moments form ferromagnetic sheets within the basal planes. The magnetic moment direction between nearest neighbour atomic planes undergo a rotation about the *c*-axis to form a spiral structure, and a schematic diagram of this is shown in figure 1. As the temperature is decreased from T_N the wavevector, τ, of the magnetic superlattice reflections decreases from approximately 0.3 to 0.17 at 20 K. At 20 K the system undergoes a first order phase transition into a conical spiral phase with a ferromagnetic component along the *c*-axis. The x-ray results were in agreement with neutron diffraction results on the same sample. In addition, the x-ray measurements provided significantly greater resolution, allowing small changes in the position and width to be measured. In 1988 Gibbs *et al* [3] performed resonant x-ray scattering

experiments around the Ho L edges and observed a resonant enhancement by a factor of 50 at the Ho L_{III} edge and resonant harmonics at the 2τ, 3τ and 4τ positions. Hannon *et al* [6] explained the results in terms of resonant electric multipole transitions at the Ho L_{III} edge. The transitions responsible for the resonant enhancement at the Ho L_{III} edge are a dipole transition from 2p–5d levels (E1) and at a lower energy a quadrupole transition from the 2p–4f level (E2). The magnetic sensitivity in the 5d band is caused by exchange interactions with the magnetically ordered 4f levels. However, the exchange splitting is significantly smaller in the 5d levels than in the 4f levels, meaning that they are broad in energy and the resonant enhancement is similar to the E2 transition from the 2p–4f levels. A significantly larger resonant enhancement would occur involving an E1 transition to the sharp 4f levels at the Ho M edges, and Hannon *et al* predicted this to be of the order of 100 r_0. Gibbs *et al* [7] successfully separated the contributions from the dipole and quadrupole transitions using polarization analysis and by analysing the energy and angular dependences. From this they determined that the E1 transition contributed to the τ and 2τ satellites, whereas the E2 transition contributed to the τ, 2τ, 3τ and 4τ satellites. Helgesen *et al* [8] studied the temperature dependence of the satellites and found that the higher order reflections decreased in intensity more rapidly than the lower order reflections.

The electronic states in which the most significant resonant enhancements are predicted are in the 3d bands in the transition metals, the 4f bands in the lanthanides and the 5f states in the actinides. However, only the M edges of the actinides lie within the normal x-ray region. To probe the 3d bands in the transition metals and 4f bands in the lanthanides, the E1 transitions occur at photon energies in the soft x-ray region i.e. at energies below 2 keV. While this is indeed possible, there are two main problems associated with carrying out diffraction in this energy region. The first is that below 2 keV the absorption of x-rays is significant and therefore the experiments must be performed in a high vacuum. Secondly, at soft x-ray energies the size of the Ewald sphere is very small and hence the volume of reciprocal space that can be accessed is extremely limited. Because of this limitation the technique can only be applied when reflections have a large d-spacing. However, recently Wilkins *et al* [9] carried out the first successful soft x-ray diffraction experiment on a single crystal of a bi-layer manganite. The system has a very long c-axis of approximately 20 Å and hence, even at the Mn L_{II} and L_{III} edges, the (0, 0, 2) Bragg reflection can be accessed. A huge resonant enhancement in the scattering was observed at the Mn L edges and this allowed the observation of the (0, 0, 1) magnetic order reflection. Such was the magnitude of the resonant enhancement at the L_{III} edge that the magnetic order reflection was easily observed. The technique is not limited to materials having a large structural d-spacing as shown by Hatton *et al* [10] in a study of $UAs_{1-x}Se_x$ at the uranium $N_{4,5}$ edges. This study showed that it was possible to access the (0, 0, 0.5) magnetic order reflection despite no Bragg peaks being accessible within the Ewald sphere.

Holmium is the prototypical system for resonant magnetic x-ray scattering. However, at the L_{III} edge it is the unfilled 5d shell that is being probed by a dipole transition and the 4f shell is probed by an E2 quadrupole transition. At the Ho M edges the 4f shell is probed directly through a strong dipole transition with no interference from higher order transitions. In this paper a study of the magnetic order in Ho at the M_{IV} and M_V edges is presented. While no Bragg peaks can be accessed in the Ewald sphere at the Ho M edges it is possible to access the long period magnetic order. Scußler-Langeheine *et al* [11] reported the successful observation of the magnetic order in an ultrathin holmium film at soft energies and used the technique to study the effect of film thickness on T_N [12]. The aim of this paper is to compare the results of this study with previous work which will determine the validity of the results from the soft x-ray scattering technique.

2. Magnetic x-ray scattering

Resonant x-ray scattering is said to occur when an incident x-ray photon is absorbed, promoting a core electron into empty states, upon which the electron and hole recombine by the emission of a photon. This process introduces anisotropic contributions to the x-ray susceptibility tensor, whereby it is possible to observe long range ordering of magnetic moments or spatially differing anisotropic electronic distributions.

The amplitude of the E1, $F^{[1]}$ scattering from a given ion is the product of a geometrical factor, which depends on the polarization of the incident ($\vec{\epsilon}$) and scattered ($\vec{\epsilon}'$) photons and a linear combination of resonance strength factors, $F_{\mathrm{L,M}}$

$$F^{[1]} \propto (\vec{\epsilon} \times \vec{\epsilon}') \cdot \vec{\hat{z}}[F_{1,1} - F_{1,-1}]. \tag{1}$$

These terms rotate the polarization of the scattered photons with respect to the incident photon polarization. To observe a finite intensity, a difference in the transition probabilities to the intermediate states is required. This can arise due to a spin polarization of the 4f states, a difference in the overlap integrals, or lifetime of the two channels. It is this term which allows for the observation of superlattice reflections due to the magnetic structure.

The $F^{[2]}$ term, on the other hand, observes long range order of anisotropic charge distributions. Here, the asphericity of the atomic electron density generates the anomalous tensor component in the scattering factor. This can be described by second rank tensors $f(\vec{r})$ invariant under the point symmetry of the unit cell. Writing $\tilde{f}(\vec{Q})$ as the Fourier transform of $f(\vec{r})$ yields

$$F^{[2]}(\vec{Q}) \propto \vec{\epsilon}' \cdot \tilde{f}(\vec{Q}) \cdot \vec{\epsilon}, \tag{2}$$

where $\vec{\epsilon}$ and $\vec{\epsilon}'$ are the electric field polarization vectors of the incident and scattered beams. This is the Tempelton–Tempelton or ATS (anisotropic tensor susceptibility) scattering.

At the Ho M edges there should be no quadrupole transition because the dominant transition is a dipole transition from the 3d–4f level and there are no allowed quadrupole transitions that occur at the same energy as this transition.

3. Experimental details

A high quality sample of holmium was grown at the University of Birmingham and it was cut so that the $\langle 0, 0, 1 \rangle$ direction was surface normal. The surface had been polished with a solution of 25% nitric acid, 25% acetic acid and 50% methanol followed by a methanol wash. This ensured the surface was of a high quality which was vital for measurements at soft energies. The measurements were performed on station 5U1 at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory UK [13]. The diffractometer is mounted in a high vacuum vessel to eliminate air absorption and operates at a pressure of approximately 10^{-6} Torr. A 300 μm slit was placed in front of the detector to increase the resolution, providing an angular resolution of 0.1°.

To determine the position of the absorption edges, drain current measurements were performed. To enable these measurements to be carried out it was necessary to electronically insulate the sample using GE varnish and a thin piece of paper. This ensures there is no electrical contact between the sample and the copper sample mount but still allows a good thermal contact with the cooling mechanism. A wire was attached to the sample using conductive silver epoxy which was attached to an ammeter to measure the drain current.

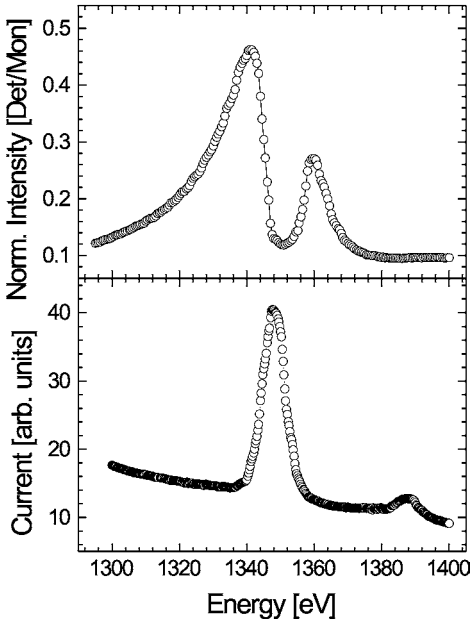

Figure 2. Energy scan at constant wavevector through the (0, 0, τ) magnetic order reflection(top panel). The drain current measurement of the sample is shown in the bottom panel. The curves are guides to the eye.

4. Results

The sample was cooled to 85 K and drain current measurements were used to determine the exact position of the holmium M_V and M_{IV} edges. From these measurements the edge positions were confirmed as 1348 and 1391 eV for the M_V and M_{IV} edges respectively. The energy was tuned to the M_{IV} and M_V edges as calculated from the drain current measurements and a search carried out for the reflections associated with the magnetic order. There was no evidence of magnetic order at any modulation at the Ho M_{IV} edge. However, at the M_V edge a very intense reflection was observed at a 2θ angle of 23.95° and a weaker reflection at a 2θ angle of 49.08°. These angles correspond to a modulation at (0, 0, 0.255) for the strong reflection and (0, 0, 0.510) for the weak reflection, and these were attributed to the τ and 2τ satellites. No evidence of the third and fourth harmonics was observed, which is expected because only the first and second harmonics are associated with the dipole transition from the 3d–4f levels at the M_V edge. A scan performed above T_N confirmed that the reflections originated from the magnetic order.

Energy scans at constant wavevector were performed on both the τ and 2τ reflections and are shown in figures 2 and 3 respectively in high resolution mode which corresponded to an instrument resolution of 2 eV. The lower panel of figure 2 shows the drain current measurement on the sample. The (0, 0, τ) reflection was not observed far away from the M_V edge but as the energy was increased towards the absorption edge there was a dramatic enhancement in the scattered intensity, with it maximizing at 1340 eV. However, as the energy was increased towards the edge the intensity decreased and reached a minimum at 1348 eV, which corresponded to the edge position indicated by the drain current. The intensity recovered as the energy was increased above the edge, maximizing at 1360 eV and decreasing above this

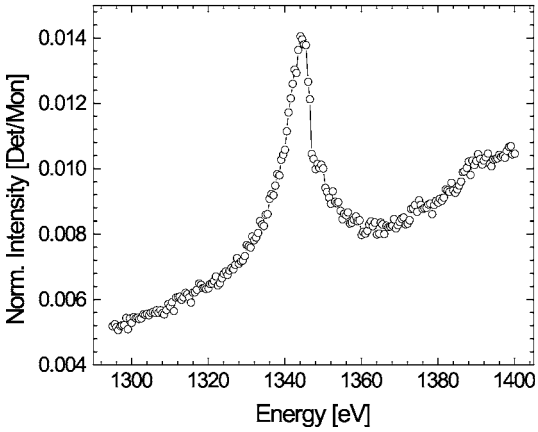

Figure 3. Energy scan at constant wavevector through the $(0, 0, 2\tau)$ magnetic order reflection. The curve is a guide to the eye.

energy. We do not believe this behaviour is a result of two separate transitions to the 4f and 5d levels. The separation of the two peaks in the energy scan is approximately 20 eV and the results at the Ho L_{III} edge have shown that the separation between the 4f and 5d levels is only 6 eV. We believe that the results observed are a result of the large photon absorption at the M_V edge. The drain current is an indication of the level of absorption and in figure 2 the intensity of the first order reflection begins to decrease at 1340 eV, corresponding to the energy where the drain current starts to increase and, hence, the absorption begins to increase. The drain current maximized at 1348 eV, corresponding to the minima in the intensity of the first order reflection, and the decrease in the drain current above 1348 eV corresponded to the recovery in the scattered intensity. From this we postulate that the data is not a result of two separate transitions. Attempts to fit the energy scan to a single peak were unsuccessful and gave an estimated linewidth for the transition of over 20 eV, which does not agree with the theory. The experiments at the L_{III} edge by Gibbs *et al* measured the FWHM of the quadrupole transition 2p–4f to be 6 eV, and the dipole transition 3d–4f at the M_V edge would be expected to show the same width because it is mainly dependent on the width of the excited states, with the influence of the core states not significant enough to explain this discrepancy. We suggest two explanations for this result: the first is that due to the effects of absorption and extinction the width of the transition is significantly broadened. The second explanation is that the absorption is large enough to mask a huge resonance that maximizes at 1345 eV, and if this could be corrected a dramatic energy resonance would be observed with a linewidth of 6 eV.

The $(0, 0, 2\tau)$ reflection was significantly weaker than the first order reflection, which is in agreement with the results observed at the L_{III} edge. The reflection was not observed far away from the absorption edge and as the energy was increased towards the absorption edge there was an enhancement in the scattered intensity that maximized at 1345 eV which is 3 eV below the absorption edge position. This is consistent with a transition to the 4f levels because the results observed at the L_{III} edge by Gibbs *et al* found the quadrupole 2p–4f transition to occur 3 eV below the edge. We believe that the 2τ reflection shows different behaviour from the τ reflection because it occurs at a higher angle which reduces the effects of absorption and extinction. The peak was fitted to a Lorentzian lineshape and the FWHM was calculated as 9.5 ± 0.4 eV. This is broader than the expected 6 eV transition to the 4f levels measured at the Ho L_{III} edge. The difference may be partly explained by the fact that the 3d states are

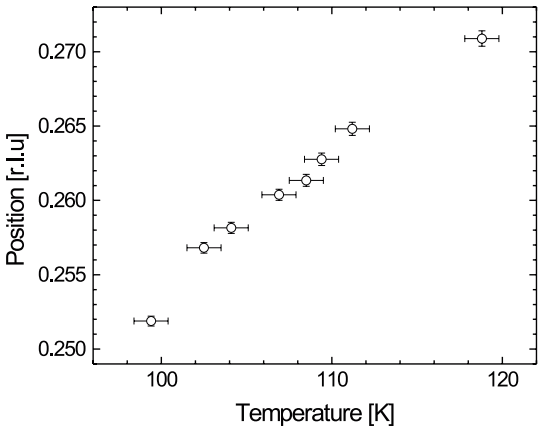

Figure 4. Corrected temperature dependence of the wavevector of the (0, 0, τ) reflection.

1 eV broader in energy than the 2p states, which could influence the linewidth, but it does not appear to be large enough to account for a 50% difference between the L and M edge results. A similar effect was observed in UAs in a comparison between the N edge results observed by Hatton *et al* [10] and the M edge results observed by Isaacs *et al* and McWhan *et al* [14, 15].

The energy scans demonstrated that the absorption at the Ho M_V edge was considerable and it was necessary to determine the surface sensitivity of the measurements. By fitting the peak width it was possible to estimate the penetration depth of the beam into the sample and this was calculated as approximately 100 Å. The earlier x-ray measurements by Helgesen *et al* [8] and Thurston *et al* [16] reported that the magnetic order was as correlated as the holmium crystal structure and our measurement is therefore a valid measurement of the penetration depth because the correlation of the magnetic order is significantly larger than the penetration depth. A penetration depth of 100 Å is very surface sensitive, particularly for the (0, 0, τ) reflection where only four periods of the magnetic order are sampled. This could explain the differences observed between the lineshapes of the τ and 2τ reflections. Even with a penetration depth of just 100 Å the τ peak was very strong, indicating that the resonant enhancement at the Ho M_V edge is huge, and is several orders of magnitude larger than that at the L_{III} edge, which is in agreement with the predicted theory.

The absorption was significant, and in order to see if this affected the behaviour of the magnetic order the integrated intensity and the wavevector were measured as a function of temperature for both the first and second order reflections. As expected there was no change in the correlation of both reflections with temperature because the measurement is limited by the penetration depth, which is considerably smaller than the correlation length of the magnetic order. The position of the τ and 2τ reflections was measured as a function of temperature. At 85 K the position of the first order reflection was calculated as (0, 0, 0.255) and a comparison with the work from Gibbs *et al* [2] revealed the wavevector to be higher than the expected (0, 0, 0.24) position. We postulate that this was caused by the relatively thick sample resulting in an offset in temperature between the sample surface and the temperature sensor, and secondly the high absorption could have caused beam heating at the sample surface. The results from Gibbs *et al* [2] were used to correct for the temperature offset; the temperature dependence of the τ reflection is shown in figure 4 and from this we estimate the errors in the temperature to be ± 1 K. The change in the modulation with temperature appeared to approximately follow that observed in earlier work, but to allow a more detailed comparison would require a temperature

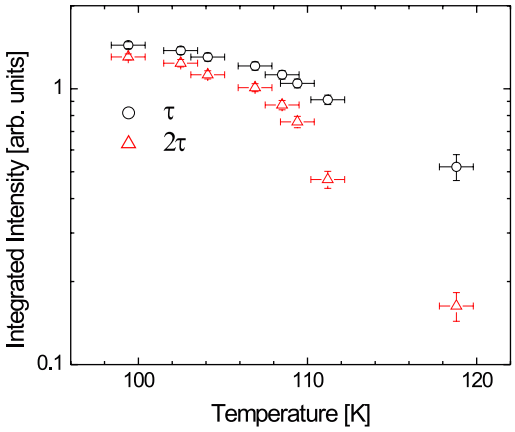

Figure 5. Comparison of the intensity at the M_V edge for the τ (circles) and 2τ (triangles) reflections. The reflections have been scaled for an easier comparison.

dependence over the whole range between 10 and 133 K which is not possible with the current equipment. The 2τ reflection showed similar behaviour but the modulation changed by double the amount of the first order reflection.

The temperature dependence of the integrated intensity for the τ and 2τ is shown in figure 5. The temperature was again corrected using the data from Gibbs *et al* [2]. Neither peak could be observed above the background above 120 K. This is lower than the accepted transition temperature of 133 K reported in earlier studies. We believe this is because the magnetic order is too weak too be observed above background. This is supported by the measured position of the τ reflection at (0, 0, 271) which is less than the modulation of approximately (0, 0, 0.28) at the transition temperature reported in earlier experiments. A comparison between the behaviour of the τ and 2τ reflections shows the integrated intensity of the second order reflection is decreasing at a greater rate than that of the first order reflection. This is in agreement with the L edge measurements by Helgesen *et al* [8] who also measured a more rapid decrease in the intensity of the second order reflection. Due to the nature of the data it was not possible to carry out accurate fitting of the temperature dependences to allow a direct comparison with the coefficients for the τ and 2τ calculated by Helgesen *et al* at the Ho L edge. However, even over the limited temperature range studied the behaviour of the integrated intensity appears to be in agreement qualitatively with the L-edge measurements.

From these observations we have demonstrated that the magnetic order displays the same behaviour at the M edge as previously observed in the neutron and non-resonant and resonant x-ray scattering studies. Due to the temperature limitation of the diffractometer it was obviously not possible to measure the magnetic order throughout the entire magnetically ordered region. However, the results have demonstrated that the behaviour of the integrated intensity and the wavevector is in approximate agreement with earlier neutron and x-ray results, even with the high absorption. However, the large absorption meant that it was not possible to measure the behaviour of the correlation of the magnetic order as it was limited by the low penetration depth.

5. Conclusions

This study has demonstrated that the soft x-ray technique can be used to study the magnetic order in holmium at the Ho M edges. However, the absorption at the holmium M edge is

considerable, with a penetration depth of only 100 Å. This means that the measurements are highly surface sensitive as only the top four magnetic layers are probed. Despite the high absorption the temperature dependence of the magnetic order was similar to that measured with neutrons and at the Ho L edge. The magnitude of the absorption made it difficult to determine the exact size of the resonant enhancement, but despite the small penetration depth significant intensity was observed at the edge, indicating that the resonant enhancement is huge and several orders of magnitude larger than that at the Ho L_{III} edge which is in agreement with the predicted theory. The study has demonstrated that the soft x-ray scattering technique can be used to study the rare earths in addition to the transition metal oxides. The resonant x-ray scattering technique is element specific and the technique would be ideal for investigating magnetic order in a system containing both a 3d metal and a rare earth metal.

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