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Dipolar excitations at the L_{III} x-ray absorption edges of the heavy rare earth metals


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We report measured dipolar asymmetry ratios at the L_{III} edges of the heavy rare earth metals. The results are compared with a first principles calculation and excellent agreement is found. A simple model of the scattering is developed, enabling us to re-interpret the resonant x-ray scattering in these materials and to identify the peaks in the asymmetry ratios with features in the spin and orbital moment densities.

The interpretation of magnetic x-ray spectroscopies at the L absorption edges of rare earth materials has been a subject of long standing controversy. Spectra consist of two main features: a large peak at an energy close to the absorption white-line (feature A), interpreted as arising from dipolar (E1) transitions coupling 2p core levels to unoccupied 5d and 6s states; a smaller peak a few eV lower (feature B), attributed to quadrupolar (E2) transitions coupling the same core levels to unoccupied 4f states [1-6]. In this paper we re-examine the dipolar/quadrupolar character of these structures.

X-ray resonant magnetic scattering (XRMS) assigns the E1 or E2 nature of spectral features through analysis of the scattered x-ray polarisation [7,8] and comparison with theory [9-11]. Resonant inelastic x-ray scattering (RIXS) assigns the E1 or E2 nature from their relative energy positions [5,6]. In x-ray magnetic circular dichroism (XMCD) assignment is achieved by modelling variations in signal with the angle between the incident x-ray polarisation and the magnetisation direction [12]. However, problems arise in the sign of signals and the relative importance of E2 ‘contamination’. Spectra show dispersive shapes which are thought to arise from exchange splitting and matrix element effects [13,14].

In this letter we report combined experimental and theoretical investigations of x-ray resonant interference scattering (XRIS) in the ferro/ferrimagnetic phases of heavy rare earths. For the heavy rare earth hexagonal crystal structures, E1-E2/M1 scattering is allowed and may contribute to asymmetry ratios. We exploit the possibility of virtually turning off the E2 signal by scattering horizontally through angles close to 90°, thus isolating E1 scattering. To investigate this further, first principles calculations were performed for both pure E1, pure E2, and total (E1 and E2) scattering in this geometry. The E1-E2 contributions were found to be two orders of magnitude smaller than the pure E1 scattering and thus can be eliminated as key contributions. We show that feature B is in fact of mixed E1
Fig 1. Top curves; field dependent energy scan for Gd. At each energy point the field was reversed many times and averaged to reduce systematic errors. Below; charge-magnetic XRIS asymmetry ratios (see equation (3)). Experimental data (cyan), first-principles x-ray scattering theory (red) and model (blue). Statistical errors are smaller than the plotted points In Tm, (with scattering angle < 90°), the asymmetry ratio reverses sign. Therefore we have simply inverted the curves for Tm in the figure. The curves consist of a dominant high energy peak and a lower energy shoulder that becomes more pronounced with increasing atomic number. The higher energy peak results from scattering off the spin moment and the lower energy peak arises from scattering from both the spin and orbital moments. The changing relative size and position of these peaks reflects the change in relative magnitude of these quantities. The zero of energy here is the L\textsubscript{III} edge which we equate to the Fermi energy.

and E2 origin in both absorption and scattering spectra and that the E1 contribution is substantial. Using both first principles scattering theory (fps) and an atomic-like model, we reproduce features A and B and thus confirm the E1 nature of our spectra. This has enabled identification of strong antiparallel hybridisation between the unoccupied 4f and 5d spin moments which provides a natural explanation for the size and dispersive line-shape observed in XMCD. A direct hybridisation between f and d states with parallel orbital moments is also identified. A changeover from magnetism dominated by f-d exchange and spin, to magnetism dominated by spin-orbit coupling (SOC) and orbital 4f and 5d magnetisations occurs around Er. However, with both the fps and the model, the Tm XRIS spectra were found to be inverted with respect to the experimental data. Examining this discrepancy suggests the possibility that in the excited state, the 4f/SOC might differ from that of the Hund’s rules ground state configuration, although we stress that assignment of an E1 contribution to feature B is independent of this possibility.

The experiments were performed at the XMaS beamline BM28 at the European Synchrotron Radiation Facility [15]. Ferri/ferrimagnetic charge-magnetic XRMS measurements were performed monitoring (300) reflections from each element, whilst scattering horizontally through angles of about 90° at their L\textsubscript{III} edges. Data were obtained through reversal of a vertical magnetic field applied along the c-axis at each point of energy scans, resulting in field dependent spectra, an example of which is given in the top panel of Fig. 1 for Gd. It is usual to present such data as an asymmetry ratio, R, as defined in eq. 3. [16] Spectra were calculated from a fully relativistic fps of XRMS [17,18]. The electronic structure of the elements was found using the fully relativistic SIC-LMTO method [19,20].

To model the XRIS spectra, we write the total E1 scattering amplitude as a sum of amplitudes due to charge scattering (subscript 0), spin (subscript S) and orbital (subscript L) magnetic scattering:

\[ f_{\text{tot}}(E) = \frac{3}{4\pi I} |\cos(2\theta)(F_{\text{0}}^* + iF_{\text{0}}') + \sin(2\theta)(F_{\text{L}}^* + iF_{\text{L}}') + iF_{\text{S}}' + iF_{\text{S}}^*| \]  

(1)

Where single (double) primes indicate the real (imaginary) part of the resonant scattering amplitudes F, and m is a unit vector in the magnetisation direction. On reversal of the magnetisation, magnetic terms in equation (1) change sign while the charge terms do not. The absorption coefficient is directly proportional to the DOS. In turn the Optical Theorem [21] states that the absorption coefficient is directly proportional to the imaginary part of the forward scattering amplitude. We therefore replace the imaginary parts of the scattering amplitudes of equation (1) with the equivalent DOS found from the electronic structure calculations and their real parts with a Kramers-Kronig transformation (KKT)[22] of these quantities. This method ignores matrix element effects which we have found to be slowly varying over the energy range of interest. It also implies that the extra transparency this model yields will lead to only a small accuracy loss. We define [10];

\[ \hat{\rho}_0 = \hat{\rho}_\uparrow + \hat{\rho}_\downarrow \text{ and } \hat{\rho}_S = \frac{1}{2}(\hat{\rho}_\uparrow - \hat{\rho}_\downarrow) \]  

(2)

as the charge and spin polarised convoluted densities of states respectively, where \( \hat{\rho} \) and (\( \hat{\rho} \)) are the spin up (down) unoccupied DOS convoluted with a Lorentzian (here, and in the fps, of width 3 eV for all elements) representing the core hole lifetime. Replacing the scattering amplitudes in equation (1) with the appropriate unoccupied DOS we arrive at;

\[ R = \frac{I_{\text{L}} - I_{\text{S}}}{I_{\text{L}} + I_{\text{S}}} = \frac{2\tan(2\theta)[P_s(\hat{\rho}_\uparrow\hat{\rho}_\downarrow - \hat{\rho}_\downarrow\hat{\rho}_\uparrow) + P_l(\hat{\rho}_0\hat{\rho}_\downarrow - \hat{\rho}_0\hat{\rho}_\uparrow)]}{\hat{\rho}_0^*\hat{\rho}_0^* + \hat{\rho}_0^*\hat{\rho}_0^*} \]  

(3)

where, \( I_i \) is the cross section for the magnetisation in one direction and \( I_i \) is for it reversed, the \( \hat{\rho} \)‘s represent the KK7’s of the DOS. \( P_s \) and \( P_l \) are the same photoelectron spin and orbital polarisations adopted in the analysis of XMCD and we have taken the simple values \( |P_s| = 1/4 \) and \( |P_l| = 3/4 \). Our theoretical and experimental approach of measuring photon scattering has significant advantage over first order methods (absorption, emission): (i) the XRIS asymmetry ratio is enhanced by a factor of 2tan(2\( \theta \)), leading to easily measurable signals; (ii) Diffraction is a highly efficient scattering mechanism leading to enhancement of the signal to noise ratio; (iii) we reference the signs of both the spin and the orbital contributions (and their real parts) to those of the charge, which enhances sensitivity; (iv) polarisation dependence allows almost complete separation of E1 and E2 events. Finally, in contrast to antiferromagnetic XRMS, no absorption correction is required.

Fig 1 shows measured XRIS asymmetry ratios at the L\textsubscript{III} edges. The spectra resemble RIXS spectra in [6], where the low energy feature was designated as E2 from its energy position. Also shown are pure E1 results of the fps and model. The experimental results have been rigidly shifted to superpose the high energy peaks with those in the calculated spectra and rescaled. In all elements the data contain an E1 peak, feature A, with a lower energy E1 shoulder/peak, feature B. For Tm, Feature A has become inverted, moreover, for the Hund’s rule ground state 4f electronic configuration (J=LS), both the fps and the model give a negative peak at low energy and a positive peak at high energy. Er also shows a dispersive line-shape for the J=LS
4f configuration. Small improvements in agreement between experiment and both calculations are observed for the J=\(|L-S|\) 4f configuration for all elements. Therefore we show the non-Hund’s rules compliant results, although we note that for Gd to Ho this makes very little difference and that even for Er and Tm, features A and B still occur at the same energies as those observed with the Hund’s rules configuration.

The E2 scattering amplitude simplifies in the adopted geometry, just one reversible magnetic term remains. The total E1+E2 asymmetry ratio leads to pure E1, pure E2 and mixed E1E2 charge magnetic interference terms. E2 charge scattering events are two orders of magnitude smaller than E1 charge scattering events. However, this is not true for E2 magnetic scattering, which is enhanced relative to E1 magnetic scattering, due to the large 4f and small 5d moments. This yields asymmetry ratios where the E1 charge-E2 magnetic term is scaled by a factor \(\cos(2\theta)\) relative to pure E1 terms. Thus for Ho, Er and Tm (20° = 96.1°, 93.3° and 89.5°) the E2 contributions are reduced by factors of 0.10, 0.06 and 0.01 respectively. For Gd, Tb, and Dy the scattering angles exceed 100° and the E2 suppression is less efficient. Clearly both the fpst and the model predict E1 scattering at energy position B for these elements, which fits the experimental data. We have performed polarisation analysis in the antiferromagnetic phases of Tb to Tm, which reveals almost pure E1 scattering in Ho, Er and Tm and sets an upper limit of the E2 contribution in Tb and Dy of a few percent [16].

Fig 2. (a) Spin polarised convoluted 5d DOS: Beyond Gd, the data are offset by -0.1 μμμμ\(eV\) with respect to the preceding element. The DOS have been convoluted with a 3 eV wide Lorentzians, to represent core hole broadening. The centre of the occupied 5d spin moments is also shown below \(E_F\), indicated by the arrows. The arrows above the \(E_F\) show the energy of the centre of the 5d spin moment closure peaks. The near vertical dashed lines mark the position of features A and B in Fig 1. (b) Orbital polarised convoluted 5d DOS: Data are scaled and offset as in (a). The dashed line represents the Hund’s rule state and the full line is for the non-Hund’s rule state.

The Hund’s rules ground state calculations give total magnetic moments in fair agreement with measured values for Gd to Tm. Exchange splitting dominates for Gd to Ho, after which SOC leads to bunching of mixed spin up/spin down states around the energies of the Lu \(j=5/2\) and 7/2 closed shell configuration. This is seen in the exchange splitting between occupied 5d spin states, which decreases from 0.63 eV in Gd to 0.04 eV in Tm. The occupied 5d spin moment (0.292 \(μμμμ\) in Gd, 0.023 \(μμμμ\) in Er and -0.026 \(μμμμ\) in Tm) is aligned with that of the 4f/s for Gd to Er but is antiparallel for Tm. They exhibit dispersive line-shapes, as seen in Fig 2(a). The positive parts of the dispersive shapes are stationary at around 1 eV above the Fermi energy for all elements. These features coincide with negative peaks in the unoccupied 4f spin moments, shifted to slightly higher energy due to the large increase in available d-states from 0 to 1 eV. The negative parts of the dispersive shapes occur at higher energies; ~6.5 eV for Gd, increasing to ~8 eV for Er, reducing to 7 eV for Tm. The stationary nature of the low energy peaks leads us to conclude that they arise from antiparallel \(f-d\) spin hybridisation. This large positive contribution to the 5d unoccupied moment must be compensated and this is the origin of the large negative part of the dispersive oscillation at high energy. In Tm, where the occupied \(d\) moment is reversed relative to that of the 4f states, this feature changes in a positive sense, as indicated by the arrows in Fig 2(a). This is also reflected in the polarity of feature A in Fig 1. We also find that the 6s unoccupied spin moment does not exhibit the same dispersive shape as the 5d/\(s\). The parts of the unoccupied 6s spin states which negatively reflect the occupied moments, are hybridised with the 5d DOS in the high energy tails of the 5d band. Clearly, this large 4f induced oscillation must be the origin of the dispersive XMCD spectra. Even if there were no \(d\)-band polarisation, this dispersive feature would be present, though its integral would be zero. In common with Kim et al.[14] we observe an increase in the size of the matrix elements as energy increases.

The 5d orbital moments are shown in Fig. 2(b). They exhibit double peaks, split by about 4 eV, for all elements except Tm. Here, the centroids of the two peaks are aligned with the centres of the 5d bands, which are at 3.5 to 5 eV for Gd to Tm. This splitting is visible in the total 5d DOS and is also apparent in the unoccupied spin moment in Fig 2 (a). We conclude that this splitting is due to the crystal field (CEF) (which is essentially unaffected by the partially filled \(f\)-shell configuration). In addition, there are negative dips in the Hund’s rules spectra (dashed lines) which are also stationary, at around 1 eV above \(E_F\) for all elements. These
features coincide with the negative peaks in the unoccupied 4f orbital moments, again, slightly shifted up in energy due to available d-states. Further, if we reverse the sign of the 4f spin orbit coupling (non-Hund’s rules configuration; solid lines), these features change sign and are pulled down in energy along with the unoccupied 4f orbital moments. We conclude that these features are due to parallel f-d orbital hybridisation. The higher energy 5d orbital moments are fairly independent of the 4f orbital configuration, as was concluded in [14]. For Er and Tm however, the hybridised 4f orbital moments dominate over the CEF splitting. Our results strongly suggest that in the presence of the 2p3/2 core hole, the 4f SOC differs from that of the Hund’s rules ground state. It has been suggested [23] that in the presence of the core hole, the 4f levels pull down in energy by ~ 3 eV (although earlier calculations found larger values[24]). As this also corresponds to calculated energy difference between the J=L+S and [L-S] configurations, it is conceivable that the core hole energy might be taken up in a reconfiguration of the 4f states, rather than a rigid shift of them during the excitation and our results support this scenario. Examination of the positions of features A and B in Fig. 2 reveals that feature A is of almost pure spin origin whereas feature B is of mixed spin and orbital origin. The correlation of peaks A and B in Fig. 1, with structure in Fig. 2(a) and Fig. 2(b) demonstrates that the dipolar asymmetry ratios at the LIII edges reflect the progression from spin-dominated Gd to orbital-dominated Er and Tm electronic structure.

This work, with analogous work at the LII edge, opens the way for quantitative measurements of quadrupole scattering contributions and the development of new sum rules.

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