

Temperature dependence of the Ho $L_{2,3}$ -edge XMCD spectra of $\text{Ho}_6\text{Fe}_{23}$

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An X-ray magnetic circular dichroism (XMCD) study performed at the Ho $L_{2,3}$ -edges in $\text{Ho}_6\text{Fe}_{23}$ as a function of temperature is presented. It is demonstrated that the anomalous temperature dependence of the Ho $L_{2,3}$ -edge XMCD signal is due to the magnetic contribution of Fe atoms. By contrast, the Ho $L_{3,3}$ -edge XMCD directly reflects the temperature dependence of the Ho magnetic moment. By combining the XMCD at both Ho $L_{2,3}$ - and $L_{3,3}$ -edges, the possibility of determining the temperature dependence of the Fe magnetic moment is demonstrated. Then, both $\mu_{\text{Ho}}(T)$ and $\mu_{\text{Fe}}(T)$ have been determined by tuning only the absorption L -edges of Ho. This result opens new possibilities of applying XMCD at these absorption edges to obtain quantitative element-specific magnetic information that is not directly obtained by other experimental tools.

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1. Introduction

X-ray magnetic circular dichroism (XMCD) has become in recent years a standard tool for studying the localized magnetism in many magnetic systems (Lovesey & Collins, 1996; Stöhr, 1999; Funk *et al.*, 2005). By incorporating element specificity, analysis of the XMCD signals in the soft X-ray range provides quantitative estimates of the magnetic moments, including the disentangling of spin and orbital contributions, in the case of localized states carrying a magnetic moment. However, the contribution of XMCD to the study of the conduction band magnetism is not so straightforward. This is the case of the XMCD at the $L_{2,3}$ -edges of the rare-earths and at the K -edge of $3d$ transition metals in which delocalized states ($5d$ and $4p$, respectively) are probed in the absorption process.

The XMCD at the rare-earth $L_{2,3}$ -edges has been a matter of study for years, especially regarding the non-negligible role of quadrupolar transitions (Lang *et al.*, 1994, 1995; Chaboy, Bartolomé *et al.*, 1998), the spin-dependence of the radial matrix elements of the dipolar transition (Wang *et al.*, 1993) and the importance of the $5d$ – $4f$ exchange interaction (Jo & Imada, 1993). All these ingredients acting at the $L_{2,3}$ XMCD spectra avoid establishing a direct relationship between the XMCD and the magnetic state of the $5d$ states. Beyond the interest in fundamental physics, this scenario casts doubts regarding whether the XMCD at these absorption edges can provide useful and quantitative information not directly attained by other experimental tools.

In this respect we have performed a longstanding study of the rare-earth $L_{2,3}$ - and transition-metal K -edges in rare-earth transition-metal intermetallic compounds (Chaboy *et al.*, 1996, 2004; Chaboy, García *et al.*, 1998; Laguna-Marco, Chaboy, Piquer *et al.*, 2005; Chaboy, Laguna-Marco, Maruyama *et al.*, 2007; Chaboy, Piquer *et al.*, 2007; Ishimatsu *et al.*, 2007; Laguna-Marco, 2007). The results of this research indicate that the study of the conduction band at these absorption edges is further complicated in these multi-component magnetic systems as both atomic species, R and T, influence the XMCD spectra recorded at the K -edge of the transition metal and at the L -edges of the rare-earth, respectively. These studies have also shown the relationship between the XMCD and the molecular field (Chaboy, Laguna-Marco *et al.*, 2007) as well as a way of experimentally determining the R($5d$)–T($3d$) hybridization (Laguna-Marco *et al.*, 2008) in these R–T compounds. Moreover, it has been recently shown that the correct interpretation of the R $L_{2,3}$ - and T K -edge XMCD signals opens the possibility of disentangling the magnetic contribution of different atomic species within the same material by using a single X-ray absorption edge (Chaboy *et al.*, 2008).

To date, most of these experiments have been performed on RT_2 Laves phase compounds in which the total magnetization of the system is dominated by the rare-earth. The question posed is to verify whether the above results are common to all R–T intermetallics independently of their stoichiometry. To this end we have performed an analysis of the temperature dependence of the XMCD signal recorded at the $L_{2,3}$ -edges of Ho in $\text{Ho}_6\text{Fe}_{23}$. The suitability of this material to the present

study resides in the fact that owing to the ferrimagnetic coupling of the Fe and Ho moments, and to the 6:23 stoichiometry, the overall magnetization of the system is determined either by the Fe sublattice or the Ho sublattice depending on the temperature range. A previous work on this system (Laguna-Marco, Chaboy & Maruyama, 2005) allows us to identify the contribution of the Fe atoms to the XMCD recorded at the L_2 -edge of Ho yielding an anomalous temperature dependence. However, detailed quantitative information on this contribution such as its relationship with the Fe magnetic moment was missed. On the basis of the results recently published (Chaboy *et al.*, 2008), we have re-investigated such anomalous behavior aiming to verify the possibility of extracting quantitative magnetic information of the different atoms (Fe and Ho) present in the material by tuning the absorption edge of a single atom (Ho). Our results show that by tuning the X-ray absorption at the $L_{2,3}$ -edges of the rare-earth it is possible to determine the temperature dependence of the magnetic moments of both Ho, $\mu_{\text{Ho}}(T)$, and Fe, $\mu_{\text{Fe}}(T)$. These results open the possibility of obtaining a quantitative magnetic characterization of complex magnetic systems by using XMCD in the hard X-ray region, including element-specific magnetometry, by tuning the X-ray absorption of a single atomic species.

2. Experimental

The R_6Fe_{23} samples (with $\text{R} = \text{Y}$ and Ho) were prepared following standard procedures (Herbst & Croat, 1984). X-ray diffraction analysis showed that all the samples were single phase (Laguna-Marco, 2007). The macroscopic magnetic measurements were performed following standard methods in magnetic fields up to 50 kOe, by using a commercial SQUID magnetometer (Quantum Design MPMS-S5).

XMCD experiments were performed at beamline BL39XU of the SPring-8 facility (Maruyama, 2001). XMCD spectra were recorded in the transmission mode at the Ho $L_{2,3}$ -edges by using the helicity-modulation technique (Suzuki *et al.*, 1998). They were recorded under the action of a 0.6 T magnetic field applied at 45° away from the incident beam direction at different fixed temperatures from room temperature down to 80 K. The sample was magnetized by an external magnetic field applied in the direction of the incident beam and the helicity was changed from positive to negative at each energy point. The XMCD spectrum corresponds to the spin-dependent absorption coefficient obtained as the difference of the absorption coefficient $\mu_c = (\mu^- - \mu^+)$ for anti-parallel, μ^- , and parallel, μ^+ , orientation of the photon helicity and the magnetic field applied to the sample. For the sake of accuracy the direction of the applied magnetic field is reversed and XMCD, now $\mu_c = (\mu^+ - \mu^-)$, is recorded again by switching the helicity. Subtraction of the XMCD spectra recorded for both field orientations cancels, if present, any spurious signal. For the measurements, homogeneous layers of the powdered samples were made by spreading fine powders of the material onto an adhesive tape. Thickness and homogeneity of the samples were optimized to obtain the best

signal-to-noise ratio, giving a total absorption jump of ~ 1 at about 150 eV above the edge. In all of the cases the origin of the energy scale, E_0 , was chosen at the inflection point of the absorption edge and the XAS spectra were normalized to the averaged absorption coefficient at high energy.

3. Results and discussion

The ferrimagnetic $\text{Ho}_6\text{Fe}_{23}$ compound exhibits a magnetization compensation phenomenon as a function of temperature which originates from the different temperature dependence of both the iron, μ_{Fe} , and Ho, μ_{Ho} , magnetic moments. In a first approach the magnetization of the compound can be described as corresponding to the addition of the magnetization of each magnetic, Fe and Ho, sublattice. At room temperature the Fe sublattice dominates the overall magnetization of the system. On cooling from room temperature, the magnetization continuously decreases up to $T_{\text{Comp}} \simeq 192$ K and then it increases for further cooling up to 4.2 K. This temperature dependence is due to the fact that the Ho magnetic moment, being ferrimagnetically coupled to that of Fe, increases faster than μ_{Fe} as the temperature decreases. Therefore the total magnetization decreases until it vanishes at T_{Comp} . On further cooling below T_{Comp} , the magnetization of the Ho sublattice prevails and the total magnetization of the system shows a continuous increase (Laguna-Marco, Chaboy & Maruyama, 2005). The Ho magnetic moment can be extracted from the magnetization measurements by assuming that the temperature dependence of the Fe sublattice in $\text{Ho}_6\text{Fe}_{23}$ corresponds to that of Y_6Fe_{23} (Herbst & Croat, 1984). In this way it has been determined that μ_{Ho} increases from $4.70\mu_{\text{B}}$ at room temperature to $9.26\mu_{\text{B}}$ at $T = 5$ K. While the relative modification of μ_{Ho} between ambient and low temperature is $\sim 97\%$, it is only $\sim 17\%$ for μ_{Fe} (from $1.61\mu_{\text{B}}$ to $1.87\mu_{\text{B}}$).

The XMCD spectra recorded at both the $L_{2,3}$ -edges of Ho are reported in Fig. 1. It should be noted that the XMCD spectra show a sign reversal below the compensation temperature, reflecting the change of the magnetic sublattice governing the sign of the total magnetization above (Fe) and below (Ho) T_{Comp} . For the sake of clarity, all the spectra are displayed with the same sign as the low-temperature ones, *i.e.* when Ho dominates the overall magnetization of the system. In the case of the Ho L_3 -edge the XMCD spectra exhibit two main features of opposite sign located, respectively, at -5 eV (A) and 3 eV (B) above the edge. This spectral shape is not modified when the temperature varies and only the amplitude of the overall signal is concerned. In this way the integration of L_3 -edge XMCD spectra yields a temperature dependence that fits well the variation of the Ho magnetic moment derived from magnetization data. This comparison is shown in Fig. 1(c) in which the variation of both XMCD integral and μ_{Ho} are plotted in relation to their room-temperature values. The same criterion will be followed hereafter to evaluate the relative variation of the signals. By contrast with the L_3 case, the spectral shape of the Ho L_2 -edge XMCD is modified as a function of temperature. At room temperature the main

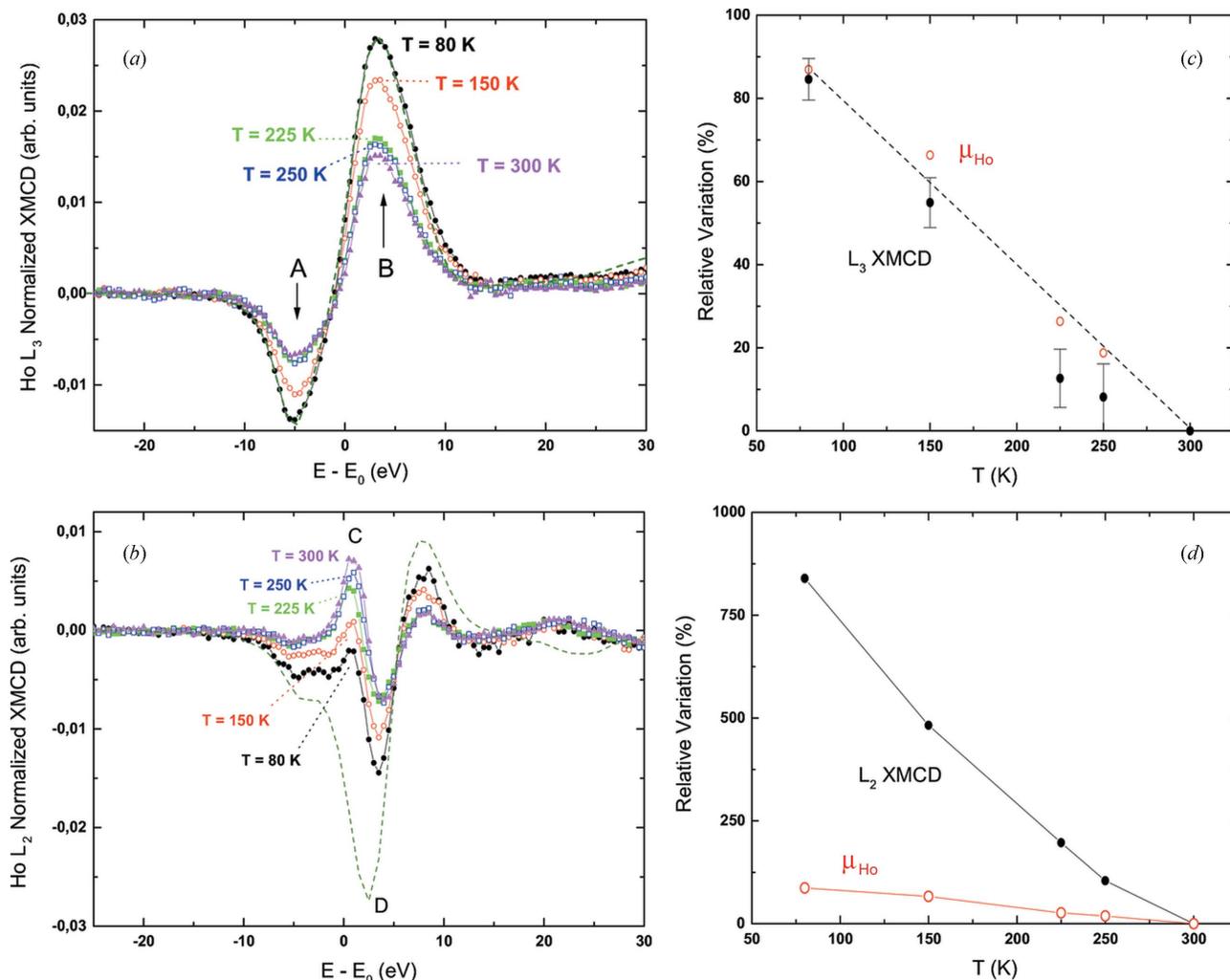


Figure 1 (a) and (b) Temperature dependence of the XMCD spectra of Ho at the L_{3-} (a) and L_{2-} edge (b) in $\text{Ho}_6\text{Fe}_{23}$: $T = 80$ K (black, filled circles), $T = 150$ K (red, open circles), $T = 225$ K (green, filled squares), $T = 250$ K (blue, open squares) and $T = 300$ K (purple, filled triangles). For the sake of comparison, the $\text{Ho } L_2$ XMCD spectrum of HoAl_2 recorded at $T = 5$ K and $H = 5$ T is also shown (dark green, dashed line) in (b). The same is done for L_3 in (a) but for the HoAl_2 signal scaled to match the amplitude of $\text{Ho}_6\text{Fe}_{23}$ at $T = 80$ K. (c) and (d) Comparison of the temperature dependence, relative to the room-temperature values, of the Ho magnetic moment, derived from magnetization data (red, open circles) and the integrated XMCD signals (black, filled circles) of the $\text{Ho } L_3$ (c) and L_2 (d) absorption edges.

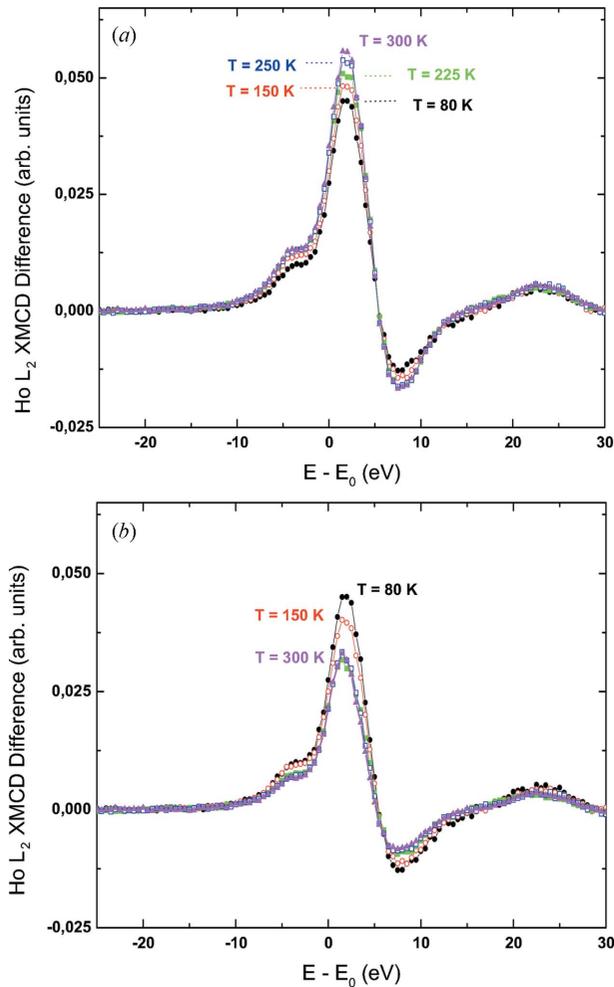
structures of the L_2 -edge XMCD spectrum are a positive peak (C) at 1 eV and a negative one (D) at ~ 3 eV above the edge. As the temperature decreases, the amplitude of the signal increases as expected from the enhancement of the Ho magnetic moment. However, the intensity of peak C shows the contrary trend and this peak is progressively depleted. As previously discussed (Laguna-Marco, Chaboy & Maruyama, 2005), this anomalous behaviour is due to the influence of the Fe sublattice magnetization even when the Ho L_2 -edge is tuned.¹ As a consequence, the integral of the XMCD signal shows a temperature dependence with a relative variation one order of magnitude greater than that expected for μ_{Ho} .

This anomalous behaviour stems from the competition of both Ho and Fe sublattice magnetization to the L_2 XMCD signal (Laguna-Marco, Chaboy & Maruyama, 2005). Indeed,

peak C is absent in the case of HoAl_2 , *i.e.* in a system in which the only magnetic contribution comes from Ho atoms. Then, our main aim is to disentangle both Fe and Ho contributions from the Ho L_2 -edge XMCD spectra as a function of temperature in order to determine both $\mu_{\text{Fe}}(T)$ and $\mu_{\text{Ho}}(T)$ from the same absorption spectra.

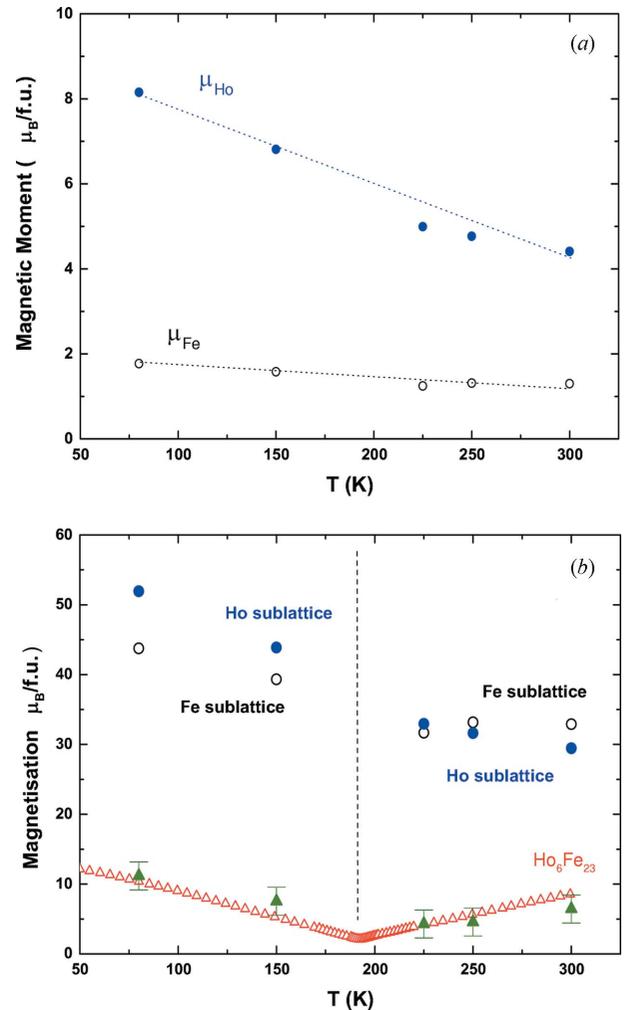
To this end we have considered the XMCD signals recorded at the Ho $L_{2,3}$ -edges in HoAl_2 at $T = 4.2$ K and under the action of an applied magnetic field $H = 5$ T. Under these experimental conditions the magnetic moment of Ho is close to its free-ion value and, consequently, one can assume that these signals would reflect the Ho contribution to the $\text{Ho}_6\text{Fe}_{23}$ L -edges spectra in the absence of any Fe contribution. However, one has to consider that, at $T = 80$ K, μ_{Ho} does not correspond to the free-ion value. Therefore, we have scaled the $\text{Ho } L_3$ XMCD of HoAl_2 to match that of $\text{Ho}_6\text{Fe}_{23}$ at $T = 80$ K, and this scaling factor has been further applied to the L_2 spectrum (see Fig. 1). By subtracting now the scaled HoAl_2

¹This contribution is not detected at the L_3 -edge XMCD. See Chaboy, Laguna-Marco, Piquer *et al.* (2007) for a detailed discussion.


Figure 2

(a) Comparison of the signal obtained after subtracting from the Ho L_2 XMCD $\text{Ho}_6\text{Fe}_{23}$ signals the XMCD spectrum of HoAl_2 after scaling to $T = 80$ K: $T = 80$ K (black, filled circles), $T = 150$ K (red, open circles), $T = 225$ K (green, filled squares), $T = 250$ K (blue, open squares) and $T = 300$ K (purple, filled triangles). (b) Same comparison as above after weighting the HoAl_2 signal with the temperature dependence observed at the Ho L_3 -edge (see text for details).

signal from the L_2 spectra of $\text{Ho}_6\text{Fe}_{23}$ the Ho contribution is cancelled and the remaining signal would correspond to the Fe contribution. The result of applying this procedure is shown in Fig. 2. The difference signal is characterized by an intense positive peak at the edge whose intensity should be proportional to the Fe magnetization. However, this procedure would only be valid at $T = 80$ K. Indeed, despite the fact that the shape of the extracted signal does not vary with temperature, the intensity of the extracted Fe contribution increases with temperature, while μ_{Fe} is expected to decrease. The reason for this discrepancy is that, as the temperature increases, μ_{Ho} decreases faster than μ_{Fe} . Therefore the Ho contribution has to be subtracted from $\text{Ho}_6\text{Fe}_{23}$ by taking into account the temperature dependence, that should be different from that of Fe. Then, we have assumed that the amplitude of the Ho L_3 XMCD signal is directly related to μ_{Ho} and, consequently, $\mu_{\text{Ho}}(T)$ is given by the temperature dependence of the XMCD amplitude at this absorption edge. In this way we considered


Figure 3

(a) Comparison of the temperature dependence of the magnetic moment of Ho (blue, filled circles) and Fe (black, open circles) extracted, respectively, from the L_3 and L_2 XMCD spectra of $\text{Ho}_6\text{Fe}_{23}$. (b) Comparison of the temperature dependence of the magnetization of $\text{Ho}_6\text{Fe}_{23}$ measured at SQUID (red, open triangles) and obtained (green, filled triangles) by using the magnetization of the Ho and Fe sublattices derived from the Ho $L_{2,3}$ -edges XMCD spectra.

that the Ho L_2 -edge XMCD signal can be decomposed as the addition of two contributions, $\text{XMCD}_{\text{Tot}}(T) = \text{XMCD}_{\text{Ho}}(T) + \text{XMCD}_{\text{Fe}}(T)$, where the Ho contribution $\text{XMCD}_{\text{Ho}}(T) = f(T) \times \text{XMCD}_{\text{HoAl}_2}(80 \text{ K})$ and the proportionality factor is derived from the intensity ratio, $f(T) = \text{XMCD}_{L_3}(T)/\text{XMCD}_{L_3}(T = 80 \text{ K})$, of the Ho L_3 XMCD spectra. After applying this procedure the intensity of the obtained signal, the Fe contribution, decreases as the temperature increases, in agreement with the expected variation of $\mu_{\text{Fe}}(T)$.

The final step here is to determine how reliable the obtained $\mu_{\text{Ho}}(T)$ and $\mu_{\text{Fe}}(T)$ temperature dependences are. At $T = 80$ K the magnetic moments of Ho and Fe are, respectively, $\mu_{\text{Ho}} = 8.15 \mu_{\text{B}}$ and $\mu_{\text{Fe}} = 1.77 \mu_{\text{B}}$, as derived from magnetization data (Laguna-Marco, Chaboy & Maruyama, 2005). By considering these values and the temperature dependence of the Ho $L_{2,3}$ -edges XMCD spectra we obtain the quantitative determination for both $\mu_{\text{Ho}}(T)$ and $\mu_{\text{Fe}}(T)$ shown in Fig. 3. These results

agree with the faster decrease of the Ho magnetic moment than that of Fe as the temperature increases. Moreover, we have compared in Fig. 3(b) the magnetization of the Ho₆Fe₂₃ compound measured by conventional magnetometry methods and built from the $\mu_{\text{Ho}}(T)$ and $\mu_{\text{Fe}}(T)$ values determined from the XMCD data. The obtained agreement supports the success of disentangling the magnetic contribution of both Fe and Ho by using only the Ho X-ray absorption edges.

4. Summary and conclusions

We have presented a systematic study of the temperature dependence of the XMCD signals recorded at the Ho $L_{2,3}$ -edges in Ho₆Fe₂₃. While the amplitude of the Ho L_{3} -edge XMCD spectra follows the variation of the Ho magnetic moment with temperature, the behaviour of the Ho L_{2} -edge XMCD signal is neither proportional to the Ho magnetic moment nor to the magnetization of the system. This anomalous behaviour has been accounted for in terms of the contribution of the Fe sublattice magnetization to the Ho L_{2} -edge XMCD signal. On the basis of the results recently published (Chaboy *et al.*, 2008) we have re-investigated such anomalous behavior aiming to verify the possibility of extracting quantitative magnetic information of the different atoms (Fe and Ho) present in the material by tuning the absorption of a single atom (Ho).

Our results show that by tuning the X-ray absorption at the $L_{2,3}$ -edges of the rare-earth as a function of temperature it is possible to determine the temperature dependence of the magnetic moments of both Ho, $\mu_{\text{Ho}}(T)$, and Fe, $\mu_{\text{Fe}}(T)$. These results open the possibility of obtaining a quantitative magnetic characterization of complex magnetic systems by using XMCD in the hard X-ray region, including element-specific magnetometry, by tuning the X-ray absorption of a single atomic species.

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