Relationship between XMCD and molecular field in rare-earth (R) transition-metal (T)

intermetallic compounds

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Abstract

This work reports an x-ray magnetic circular dichroism (XMCD) study performed at the rare-earth $L_{2,3}$ edges in several rare-earth transition-metal RT_2 compounds (T = Fe, Co and Al). The transition metal contributes to the XMCD of the rare earth recorded at the L_2 edge while no influence is detected at the L_3 edge. This contribution shows the same spectral shape for both light and heavy rare earths and its amplitude reflects the sign and the magnitude of the magnetic moment of the transition metal. The results here presented point out that this contribution is associated with the molecular field due to the transition metal acting at the rare-earth sites.

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

1. Introduction

In the last years the advent of new synchrotron radiation sources has led to the development of magnetic studies on microscopic level by using x-ray core-level spectroscopies such as x-ray circular magnetic dichroism (XMCD). The main characteristic of XMCD resides in its atomic selectivity, that, combined with the so called sum-rules [1, 2], leads to the possibility of obtaining an element-specific quantitative determination of spin and orbital magnetic moments.

Nowadays, XMCD is commonly used to probe the spin and orbital magnetic moments of the transition-metal (T) d states in different systems [3]. However, the same does not hold for the 5d states of the rare earths (R). Indeed, while XMCD can satisfactorily account for the cases in which the final states are localized, T 3d ($L_{2,3}$ edges) and R 4f ($M_{4,5}$), the mechanism governing the XMCD for cases in which the final state is delocalized, T 4p (K edge) and R 5d ($L_{2,3}$ edges), is still unclear. Solving this problem is specially important in connection to the basic and applied research in the field of R–T intermetallic compounds. The intrinsic magnetic

properties of these materials are determined by the exchange interaction between the R-4f and T-3d electrons. This interaction takes place through the T(3d)–R(5d) hybridization [4–6] and, consequently, the magnetic characterization of the R-5d states is required. However, the response of the 5d conduction electrons to standard tools is masked by that of the 4f electrons. Within this scenario, XMCD should offer the possibility of disentangling the magnetic contribution of the 5d and 4f states if the full understanding of the XMCD at the $L_{2,3}$ spectra of the rare earths is achieved. In this respect, recent theoretical works suggest the need of including the hybridization between the R-5d and Fe-3d bands to account for the R-$L_{2,3}$ XMCD in R–Fe intermetallics [7, 8]. However, hybridization is *ad hoc* incorporated in these models, thus acting as a fitting parameter.

This work is aimed to get a deeper insight on the interpretation of the $L_{2,3}$-edge XMCD spectra of the rare earths. To this end we have performed a study of the R-$L_{2,3}$ XMCD in RT$_2$ compounds in which the magnetic properties of the transition metal (Fe, Co and Al), and thus the T(3d)–R(5d) hybridization, are modified. In this way, we have determined that the transition metal contributes to the L_2-edge XMCD spectrum of the rare earth. We have identified and isolated this contribution from the spectra, showing that it reflects the magnitude of the transition-metal magnetic moment as well as the sign of its coupling (ferro- or ferrimagnetic) to the rare-earth one. These results are discussed in terms of the relationship between XMCD and the molecular field acting at the rare-earth sites.

2. Experimental details

ErAl$_2$, ErCo$_2$, ErFe$_2$, (Nd$_{0.8}$Lu$_{0.2}$)Al$_2$, NdCo$_2$, Nd(Fe$_{0.25}$Al$_{0.75}$)$_2$ and (Gd$_{0.75}$Lu$_{0.25}$)Al$_2$ samples were prepared by arc-melting the pure elements under Ar protective atmosphere. The ingots were annealed at 850 °C for one week. Structural characterization was performed at room temperature by means of powder x-ray diffraction by using a rotating-anode Rigaku diffractometer in the Bragg–Brentano geometry, with Cu Kα radiation. All the samples are single phase and show the MgCu$_2$-type (C15) Laves structure [9].

XMCD experiments were performed at beamline BL39XU of the SPring-8 Facility [10]. XMCD spectra were recorded in the transmission mode at the rare-earth $L_{2,3}$ edges by using the helicity-modulation technique [11]. The sample is magnetized by an external magnetic field applied in the direction of the incident beam and the helicity is changed from positive to negative 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 antiparallel, 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 the XMCD, now $\mu_c = (\mu^+ - \mu^-)$, is recorded again by switching the helicity. The 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 on an adhesive tape. Thickness and homogeneity of the samples were optimized to obtain the best signal-to-noise ratio. The XMCD spectra were recorded at $T = 5$ K and $\mu_0 H = 5$ T. In all cases, the origin of the energy scale 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 comparison of the XMCD signals recorded at the Er $L_{2,3}$ edges in the case of ErAl$_2$, ErCo$_2$ and ErFe$_2$ is reported in figure 1. In the case of the Er L_3 edge, all the ErT$_2$ compounds exhibit
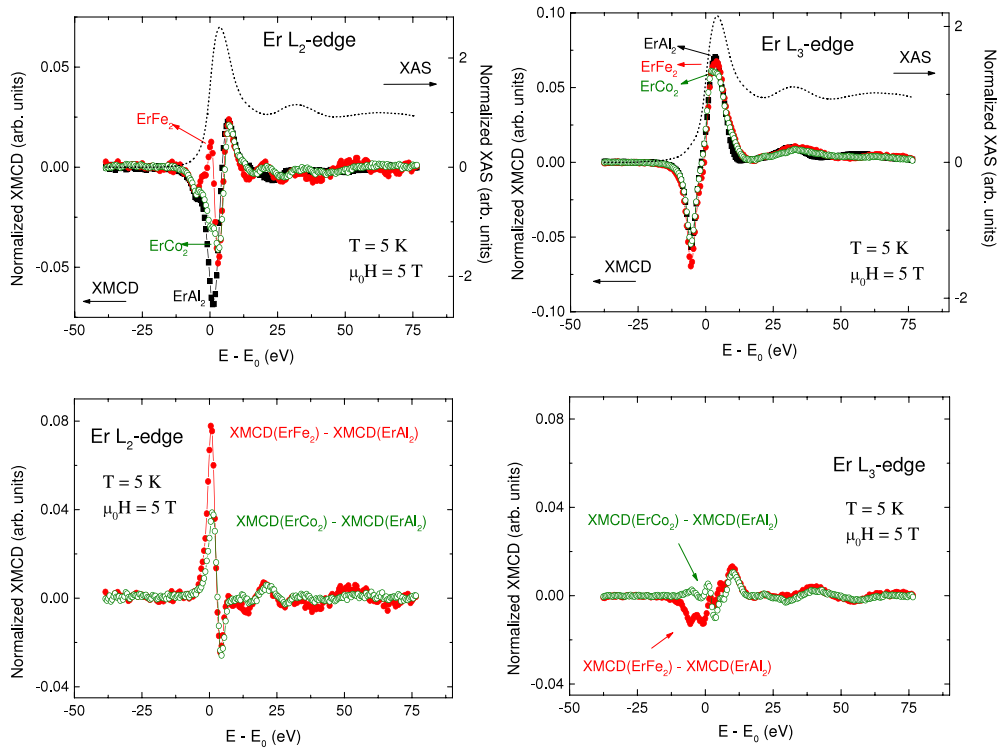
Figure 1. Top panel: normalized XMCD spectra recorded at the Er L_2 (left) and L_3 edge (right) of ErAl$_2$ (black, ■), ErCo$_2$ (green, ○) and ErFe$_2$ (red, ●). The spectra have been recorded at $T = 5$ K and $\mu_0 H = 5$ T. For the sake of clarity, the normalized Er $L_{2,3}$-edge XAS spectra of ErAl$_2$ are shown (dotted line). Bottom panel: comparison of the difference between the Er L_2- (left) and L_3-edge (right) normalized XMCD spectra of ErCo$_2$ (green, ○) and ErFe$_2$ (red, ●) after subtracting the XMCD spectrum of ErAl$_2$ at the same absorption edge.

a similar XMCD spectrum. The dichroic signal is composed of a negative peak at ~ 5.5 eV below the edge, and a positive one at 3.5 eV above the edge. The change of the transition metal does not affect the spectral shape and only the intensity ratio between the positive and the negative peaks is affected. In the case of ErAl$_2$ this ratio is ~ 1.23, being 1.1 for ErCo$_2$ and 0.94 for ErFe$_2$. However, this behaviour is dramatically changed at the Er L_2 edge. The XMCD spectrum measured at the Er L_2 edge in ErAl$_2$ shows a main negative peak centred at ~ 1 eV above the edge and a smaller positive peak at higher energy ($E - E_0 \sim 7$ eV). When a magnetic (Co or Fe) 3d metal is placed in the ErT$_2$ lattice the positive peak remains invariable. By contrast, both the shape and the amplitude of the negative contribution at $E - E_0 \sim 1$ eV are modified with respect to those of ErAl$_2$. In the case of ErCo$_2$ the amplitude of the main negative peak is about half of that of ErAl$_2$ and, in addition, this feature shows two components instead of the single negative peak in ErAl$_2$. This modification is even more marked in the case of ErFe$_2$, in which the sign of the spectral feature close to the edge changes to positive, giving rise to the appearance of a positive peak at $E - E_0 = 0.5$ eV in contrast to the single negative peak of ErAl$_2$.

These results indicate that the magnetic character of the transition metal affects the XMCD spectra of erbium even when they are recorded at the L-absorption edges of the rare earth. While the effect of the magnetism of the transition metal in ErT$_2$ is notorious in the L_2-edge

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XMCD spectra, no significant effect is detected on the XMCD recorded at the Er L_3 edge. This influence can be highlighted in the ErT_2 compounds by subtracting the XMCD spectra of $ErAl_2$. The magnetism of $ErAl_2$ is associated with the Er magnetic moment, while both Er and the transition-metal magnetic moments are competing in $ErCo_2$ and $ErFe_2$. Therefore, $ErAl_2$ can be regarded as the compound in which the Er $L_{2,3}$-edge dichroic spectra are free of the influence of the transition metal. Bearing in mind that the XMCD was recorded at low temperature ($T = 5$ K) and under the action of an applied magnetic field of 5 T, it is fair to assume that the magnetic moment of Er, μ_{Er}, is similar in all the studied compounds. Under this assumption the subtraction of the XMCD of $ErAl_2$ at both L_2 and L_3 edges from those of $ErCo_2$ and $ErFe_2$ yields the modification originated by the additional contribution of the transition metal to the Er XMCD at these edges. The result of this procedure is reported in the bottom panel of figure 1. In the case of the Er L_2 edge the extracted signal shows a sharp positive peak at the edge. While its shape is the same for both compounds, the intensity of this peak for $ErFe_2$ is twice that for $ErCo_2$. By contrast, the same procedure followed at the Er L_3 edge does not return a significant signal. The remanent signal after subtraction of the $ErAl_2$ spectrum is one order of magnitude smaller than that found at the L_2 edge.

These results are in agreement with previous reports suggesting the influence of Fe in the $L_{2,3}$-edge XMCD spectra of several intermetallic materials [12, 13]. On the other hand, the study of the temperature dependence of the XMCD spectra at both the Fe K edge and Ho $L_{2,3}$ edges in Ho_6Fe_{23} allowed the identification of a Ho contribution to the Fe K-edge XMCD signals and, conversely, from Fe ions to the Ho $L_{2,3}$ XMCD spectra. The existence of such contributions was tentatively addressed to the role of the Fe(3d)–Ho(5d) hybridization. More recently, this subject was faced in the case of the $R(Al_{1-x}Fe_x)_2$ compounds with R = Gd, Dy and Ho [14, 15]. This work applied the same procedure as above to isolate the additional contribution to the rare-earth L_2 XMCD. It was shown that the intensity of the extracted signal increases with the Fe content, i.e. with the number of Fe atoms surrounding the absorbing lanthanide ion. More interestingly, this work shows that the shape of the isolated signal is the same no matter what the rare earth and, in addition, it is kept unmodified with varying the Fe content. Therefore, it was addressed to a magnetic contribution of Fe atoms to the rare-earth XMCD. The results obtained on $ErFe_2$ support the above hypothesis. In addition, the differences found between $ErFe_2$ and $ErCo_2$ indicate that the extracted contribution is linked to the magnetic moment of the transition metal and not only to the number of T atoms surrounding the absorber. Indeed, the intensity of the isolated signal in $ErFe_2$ is twice that of $ErCo_2$, showing a good agreement with the different value of the magnetic moment of Fe ($\sim$1.23 μ_B) and Co ($\sim$0.67 μ_B) in these compounds [16–19].

As summarized above, the presence of a transition-metal contribution to the XMCD L_2 spectra of the rare earth has been identified in the case of heavy rare earths. However, to our knowledge, no report exists regarding its occurrence in the case of the light rare earths. In principle, similar behaviour should occur if this *extra* contribution is due to the Fe(3d)–R(5d) hybridization. Aiming to clarify this point, we have recorded the XMCD at the $L_{2,3}$ edges of Nd in several Laves-phase compounds showing ferromagnetic behaviour: $NdCo_2$ ($T_C = 100$ K), $Nd(Fe_{0.25}Al_{0.75})_2$ (65 K) and $(Nd_{0.8}Lu_{0.2})Al_2$ (63 K) [9]. The XMCD signals recorded in the same experimental conditions as the Er ones are displayed in figure 2. The Nd L_2-edge XMCD spectrum shows in all cases a main positive peak centred at 2 eV above the edge. Likewise, the shape profile of the Nd L_3-edge XMCD is similar for all the compounds, showing two negative peaks at energies of -5 and 3 eV relative to the absorption edge. In the case of the L_2 spectra the amplitude of the signal is maximum for the compound in which the transition metal is non-magnetic and it decreases by 20% and 33% for the compounds with Co and Fe, respectively. By contrast, the L_3 XMCD signal is less affected by the substitution. No
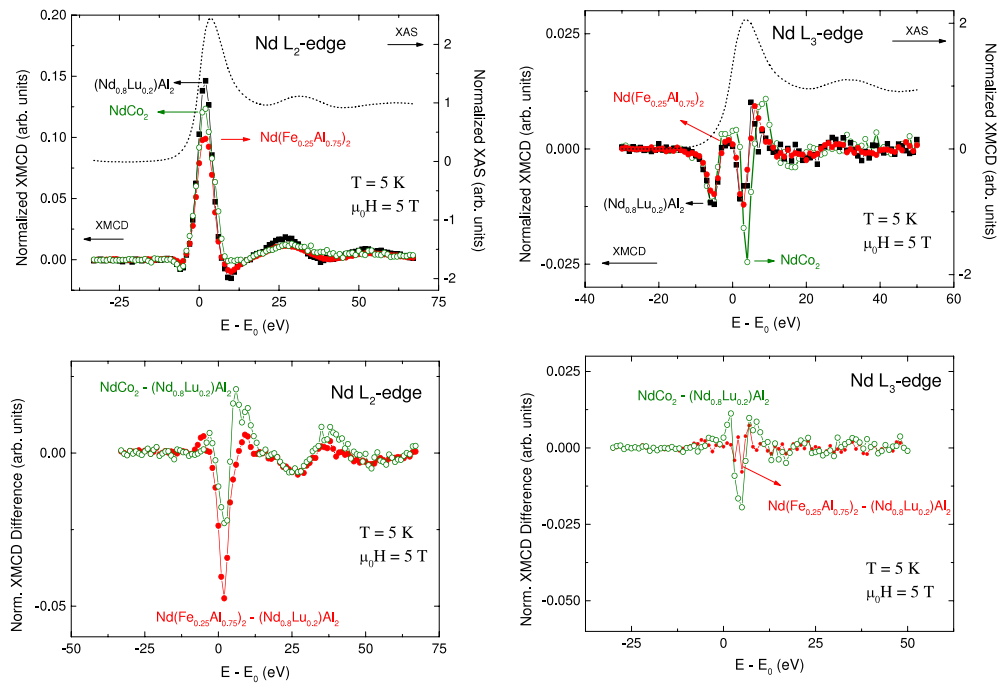
Figure 2. Top panel: normalized XMCD spectra recorded at the Nd L_2 (left) and L_3 edge (right) of $(Nd_{0.8}Lu_{0.2})Al_2$ (black, ■), $NdCo_2$ (green, ○) and $Nd(Fe_{0.25}Al_{0.75})_2$ (red, ●). The spectra have been recorded at $T = 5$ K and $\mu_0 H = 5$ T. For the sake of clarity, the normalized Nd $L_{2,3}$-edge XAS spectra of $(Nd_{0.8}Lu_{0.2})Al_2$ are shown (dotted line). Bottom panel: comparison of the difference between the Nd L_2- (left) and L_3-edge (right) normalized XMCD spectra of $NdCo_2$ (green, ○) and $Nd(Fe_{0.25}Al_{0.75})_2$ (red, ●) after subtracting the XMCD spectrum of $(Nd_{0.8}Lu_{0.2})Al_2$ at the same absorption edge.

significant difference is found regarding the amplitude of the first negative peak, and only the intensity of the second negative peak increases in the case of $NdCo_2$. This enhancement could be expected on the basis of the greater value of the magnetization of $NdCo_2$ (3.7 μ_B) with respect to that of the $Nd(Fe_{0.25}Al_{0.75})_2$ (2.2 μ_B) and $(Nd_{0.8}Lu_{0.2})Al_2$ (1.7 μ_B) compounds. However, it is difficult to reconcile this behaviour with that found at the L_2 edge in which the highest XMCD amplitude corresponds to the compound showing the smallest magnetization. These results point out the anomalous behaviour of the L_2-edge XMCD also for the light rare-earth compounds. Consequently, we have applied the same procedure as for the Er case to investigate the origin of such behaviour. We have subtracted the Nd $L_{2,3}$-edge XMCD spectra of $(Nd_{0.8}Lu_{0.2})Al_2$ from those of $NdCo_2$ and $Nd(Fe_{0.25}Al_{0.75})_2$ at the same absorption edges. As shown in figure 2 (lower panel), the results resemble those found at the Er $L_{2,3}$ edges. In the case of the Nd L_2 edge, the isolated signals show a main negative peak centred at ∼2 eV above the edge, while this difference is clearly less significative at the L_3 edge. It is worth mentioning that the intensity of the isolated signal for Fe is twice that for Co, as found in the case of the Er compounds.

These results point out that (i) there is also a contribution of the transition metal (T contribution) to the L_2 XMCD spectra of the light rare earths, (ii) as for the heavy ones, this contribution is not detected in the XMCD at the L_3 absorption edge, (iii) the shape of the isolated T contribution is the same for both light and heavy rare earths and (iv) the intensity of

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the T contribution is greater (about twice) for RFe_2 than for RCo_2 compounds no matter what the nature (light or heavy) of the rare earth. This factor of two resembles the ratio between the magnetic moments of Fe and Co in this class of materials [20, 21]. Finally, it should be noted that, despite the close similarity among the T signals isolated from the L_2-edge XMCD spectra of both Nd and Er, the sign is the opposite. As we shall discuss in the next section, this result constitutes an unambiguous probe of the contribution of the transition metal to the rare-earth XMCD, reflecting the magnitude of the magnetic moment, μ_T, as well as its magnetic coupling (ferro–ferrimagnetic) to the rare-earth one, μ_R.

The sign of the XMCD spectra indicates the orientation of the magnetic moment of the states that are being probed, with respect to the magnetization of the system. Therefore, XMCD reflects the coupling among the magnetic moments of the different atomic species present in the material. The early model formulated by Schütz and co-workers [22, 23] (typically referred to as the two-step model) shows that the XMCD spectrum reflects the difference in the density of empty states with different spin moments. This model has been successfully applied to the $L_{2,3}$ edges of 5d impurities in iron and for the 3d states of transition metals [3, 23–25].

However, this model fails to account for the $L_{2,3}$-edge XMCD spectra of the rare earths. Indeed, the analysis of the XMCD signals of Gd and Tb metal according to the Schütz's model yields that there is a large density of unoccupied spin-up states at and above the Fermi energy. Consequently, the derived 5d spin would be antiparallel to the 4f spin, which is in contradiction with the current knowledge, both experimental and theoretical, of the parallel coupling between the 4f and 5d spin moments in the lanthanides [4–6].

This is illustrated in figure 3, where the Gd $L_{2,3}$ XMCD spectra of $Gd_{0.75}Lu_{0.25}Al_2$ are shown. The negative sign of the L_2 edge indicates that the spin of the 5d states is parallel to the magnetization. However, the magnetization and the 4f spin of Gd are antiparallel. Then, the spins of the 5d and 4f states should be antiparallel according to the XMCD data. The same wrong results are found in the case of the Er and Nd $L_{2,3}$ XMCD spectra reported, respectively, in figures 1 and 2. In the case of Nd, the positive sign of the XMCD indicates that the 5d spin should be antiparallel to the magnetization, while the 4f spin is parallel to the magnetization because Nd is a light rare earth. Therefore, it is found that the sign of the R-5d magnetic moment derived from the XMCD is opposite to the expected one for both light and heavy rare earths. This contradiction was explained by Wang *et al* [26] by taking into account the spin dependence of the matrix elements previously neglected. Indeed, these calculations show that there are indeed more unoccupied spin-down states above the Fermi level. However, even though there are fewer spin-up states above the Fermi level, the matrix elements for transitions to spin-up bands are larger and cause the spectra to be dominated by spin-up transitions. The reason for this significant spin dependence of the matrix elements can be found in the radial part of the wave unctions for the 5d conduction electrons [27]. The spin-up 5d radial functions are *pulled in* relative to the spin-down functions because of their stronger exchange interaction with the localized 4f orbitals. This *pulling in* causes the 5d radial functions to have a significantly larger amplitude in the region of the 2p radial function.

However, the $L_{2,3}$ XMCD returns the right sign when the rare earth does not exhibit a 4f magnetic moment and the 5d spin is induced by the transition metal. This is the case of the Lu $L_{2,3}$ XMCD in $LuFe_2$. As shown in figure 3, strong XMCD signals are found at the the Lu $L_{2,3}$ edges, which point out that Lu bears a magnetic moment. This magnetic moment, theoretically predicted [28, 29], is antiparallel to that of Fe due to the universal coupling mechanism found in the R–T intermetallic compounds [4]. In these compounds, the R-5d and the T-3d spins are always antiparallel, while the intra-atomic 4f–5d exchange interaction renders parallel both R-4f and R-5d spins. As a consequence, the R and T magnetic moments are ferromagnetically (antiferromagnetically) coupled for light (heavy) rare earths [5, 6]. The
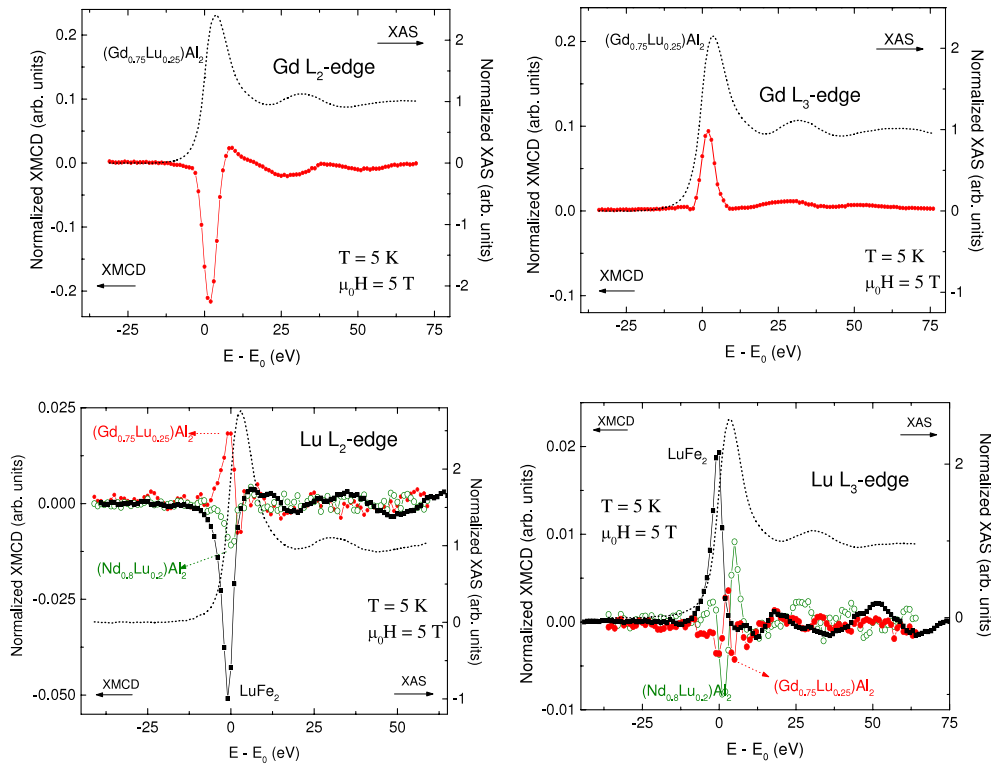
Figure 3. Top panel: normalized XMCD spectra recorded at the Gd L_2 (left) and L_3 edge (right) of $(Gd_{0.75}Lu_{0.25})Al_2$ (red, ●). The dotted lines corresponds to the normalized XAS spectra. Bottom panel: normalized XMCD spectra recorded at the Lu L_2 (left) and L_3 edge (right) in the case of $LuFe_2$ (black, ■), $(Gd_{0.75}Lu_{0.25})Al_2$ (red, ●) and $Nd_{0.8}Lu_{0.2}Al_2$ (green, ○). The dotted lines corresponds to the normalized XAS spectra of $LuFe_2$.

negative sign of the Lu L_2 signal indicates that the 5d spin is parallel to the magnetization and, consequently, the S_{5d} and S_{3d} spins are antiparallel, in agreement with the general R–T coupling scheme.

We have investigated whether the Lu $L_{2,3}$ XMCD also returns the right sign of the 5d spin when it stems from the interatomic exchange interaction with another rare earth showing a localized 4f moment. To this end we have recorded the Lu XMCD in both $Gd_{0.75}Lu_{0.25}Al_2$ and $Nd_{0.8}Lu_{0.2}Al_2$ compounds. In the case of the Nd compound, the magnetization is parallel to the Nd 4f spin while it is antiparallel for Gd. As shown in figure 3, the sign of the Lu L_2 edge is negative for $Nd_{0.8}Lu_{0.2}Al_2$, indicating that the 5d spin is parallel to the magnetization, and thus to both the 4f and 5d spins of Nd. In the case of $Gd_{0.75}Lu_{0.25}Al_2$ the positive sign of the signal indicates that the 5d spin of Lu is antiparallel to the magnetization, i.e. parallel to the Gd 4f and 5d spins.

These results suggest that if the polarization of the rare-earth 5d states stems from an interatomic interaction, the rare-earth $L_{2,3}$-edge XMCD returns the right sign, i.e. the right magnetic coupling. In contrast, the opposite occurs when the 5d polarization is due to the intra-atomic 4f–5d exchange. Then, we have studied the sign of the contribution of the transition metal to the rare-earth L_2 XMCD spectra. We have proposed that this contribution is due to the Fe(3d)–R(5d) hybridization. Then, after isolating it from the XMCD spectra, one should
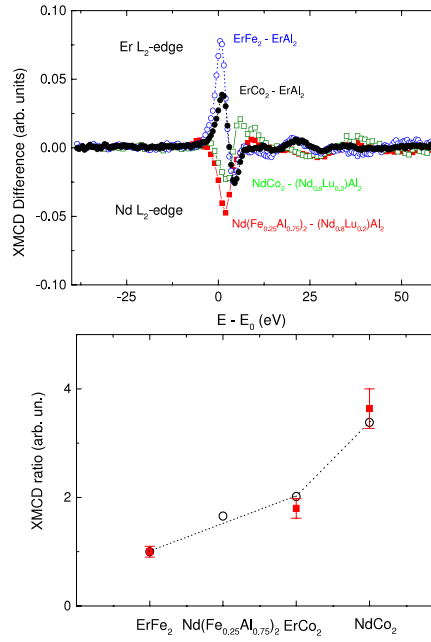
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Figure 4. Top panel: comparison of the transition-metal contribution to the Er and Nd L_2-edge XMCD in $ErFe_2$ (blue, ○), $ErCo_2$ (black, ●), $NdCo_2$ (green, □) and $Nd(Fe_{0.25}Al_{0.75})_2$ (red, ■). Bottom panel: comparison of the intensity of the extracted T contribution (black, ○) and the molecular-field analysis (red, ■) (see the text for details).

expect that it behaves as the Lu XMCD signals, i.e. showing the right sign of the 5d spin. In the case of the Er compounds (see figure 4) the isolated signals are positive, which means that the 5d spin is antiparallel to the magnetization and thus parallel to the Er 4f spin, as theoretically expected. Similarly, the signals extracted from the Nd L_2 edge are negative and thus the 5d spin is parallel to the magnetization and to the Nd 4f spin.

These results clearly indicate the influence of the interatomic polarization of the 5d states by the surrounding atoms. Therefore, we have investigated if it is possible to establish a relationship between the T contribution to the rare-earth $L_{2,3}$-edge XMCD and the molecular field acting on the absorbing sites.

Within a mean-field approach, the R–T exchange interaction is described by molecular fields that are acting on the R and T moments. In a two-sublattice model, the effective field acting on the rare-earth moments can be written as $B_{mol} = n_{RT}M_T + n_{RR}M_R$, where M_R (M_T) is the magnetic moment per formula unit of the R (T) sublattice, n_{RT} is the intersublattice molecular-field coefficient and n_{RR} is the intra-sublattice molecular-field coefficient. The T contribution has been isolated from the XMCD by subtracting that of the corresponding RAl_2 compound. In a first approach this procedure is equivalent to cancelling the $n_{RR}M_R$ contribution to the molecular field acting at the rare-earth sites. If this is the case, the intensity of the extracted signals would be proportional to $n_{RT}M_T$, i.e. to the molecular field that the transition metal induces at the rare-earth sites. Therefore, we have compared in figure 4 the intensity of the XMCD T contribution and the $n_{RT}M_T$ term of the molecular field. For each compound, we have used the n_{RT} coefficients, representing the different exchange interactions between spin moments, reported in [30]. The agreement shown in the figure gives support to our hypothesis regarding the relationship between the XMCD and the molecular field acting on the absorbing sites.

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We have tested the case of $Nd(Fe_{0.25}Al_{0.75})_2$. For this compound no $n_{RT}M_T$ data are available. Then, we have derived it from the experimental intensity of the XMCD signals. We have assumed that the intensity ratio $XMCD(RT_2)/XMCD(R'T'_2)$ of the extracted T contributions is proportional to $n_{RT}M_T/n'_{R'T'}M'_T$. In this way, we have obtained $n_{RT}M_T$ for $Nd(Fe_{0.25}Al_{0.75})_2$ from the XMCD ratio between the signals of $ErFe_2$ and of this compound. The obtained $n_{RT}M_T$ value has been tested in relation to $NdCo_2$. The experimental XMCD ratio (referred to the isolated T contributions) between $Nd(Fe_{0.25}Al_{0.75})_2$ and $NdCo_2$ yields 2.2. This value compares well with the ratio, 2.04, of the molecular field for both compounds obtained by using the $n_{RT}M_T$ derived above. Finally, we have extended this analysis to the case of the Lu L_2-edge XMCD spectra of both $Gd_{0.75}Lu_{0.25}Al_2$ and $Nd_{0.8}Lu_{0.2}Al_2$ compounds. According to our hypothesis, the XMCD signal should be proportional to the molecular field, $n_{LuR'}M'_R$, due to the magnetic moments of the magnetic rare-earth counterpart (R' = Gd and Nd). By using the values of the molecular field from [31, 32] one obtains a ratio of 1.71 that is in good agreement with the value of 1.64 obtained from the intensity ratio of the XMCD signals.

A final comment is deserved by the different contribution of the transition metal to the XMCD recorded at the L_2 and L_3 absorption edges of the rare earths. As discussed above the inadequacy of the naive model of Schütz *et al* [22] to account for the XMCD at the $L_{2,3}$ edges of the rare earths was explained in terms of the spin dependence of the matrix elements of the dipolar transition [26]. Further works by Jo and Imada [33] and Matsuyama *et al* [34, 35] show the need of including the full 5d–4f exchange interaction that leads to a spin- and orbital-dependent enhancement of the 2p–5d dipole matrix element through the contraction of the radial part of the 5d orbits. The enhancement of the matrix element also depends on the 5d occupation number, and since this is determined according to the energy it increases if the state has lower energy [35]. This is in agreement with the results of Giorgetti *et al* [12], who have proposed that in Er compounds the different behaviour of the XMCD spectra at the L_2 and L_3 edges is due to the fact that the $5d_{3/2}$ subband is more affected by the presence of the transition metal than the $5d_{5/2}$ subband. It should be noted that while both $2p_{3/2} \rightarrow 5d_{3/2}$ and $2p_{3/2} \rightarrow 5d_{5/2}$ transitions are allowed at the L_3 edge only transitions to the $5d_{3/2}$ states are allowed at the L_2 edge ($2p_{1/2} \rightarrow 5d_{3/2}$). Accordingly, the branching ratio, defined as the fraction of the total line strength going to a given j ($5d_{3/2}$ or $5d_{5/2}$) manifold, is given by the statistical value, i.e. the fraction of final-state levels in that manifold. However, early observations reported the deviation of the branching ratio from its statistical value in the case of the $L_{2,3}$ absorption edges of the rare earths and 5d transition metals [36, 37]. Indeed, Lytle *et al* suggested that at the rare-earth $L_{2,3}$ absorption the transition is not just 2p to 5d but involves the 4f electrons as well [36]. This fact was theoretically accounted for by Thole and van der Laan by showing that the branching ratio depends on both the valence band spin–orbit interaction and the electrostatic interactions in the final state [38–40]. In this way, the deviation of the branching ratio arising from the relative occupations of the $5d_{3/2}$ and $5d_{5/2}$ levels has been cast into a spin–orbit sum rule [38–40]. Within this frame our results, showing that this is a general trend in R–T intermetallics no matter whether light or heavy rare earths are concerned, gives support to the above hypothesis suggesting that the $5d_{3/2}$ subband is more affected by the presence of the transition metal than the $5d_{5/2}$ one. Consequently, they suggest that the XMCD at the rare-earth L_2 edge reflects the R–T (5d–3d) hybridization, while this is hindered by the strong influence of the 4f states at the L_3 edge.

4. Summary and conclusions

We have reported on an XMCD study performed at the rare-earth $L_{2,3}$ edges in rare-earth transition-metal RT_2 compounds (T = Fe, Co and Al). The analysis of the R L_2-edge XMCD

spectra shows the presence of a magnetic contribution coming from the transition metal even when the rare earth is probed. Such a T contribution is not detected at the L_3 edge.

The T contribution has been isolated and extracted from the experimental XMCD spectra. It shows the same spectral shape for both light and heavy rare earths, and its amplitude reflects the sign and the magnitude of the magnetic moment of the transition metal.

These results support previous theoretical works suggesting the need of considering the R(5d)–T(3d) hybridization to account for the R-$L_{2,3}$ XMCD in R–T intermetallic compounds. Moreover, we have established a direct relationship between the T contribution and the molecular field due to the transition metal acting at the rare-earth sites. These experimental findings provide a deeper insight on the interpretation of the $L_{2,3}$-edge XMCD spectra of the rare earths. Indeed, our results suggest that if the polarization of the rare-earth 5d states stems from an interatomic interaction, the rare-earth $L_{2,3}$-edge XMCD returns the right sign of the magnetic coupling, while the contrary occurs when the 5d polarization is due to the intra-atomic 4f–5d exchange.

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