Competing effects in the magnetic polarization of non-magnetic atoms.

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Abstract.
The magnetic polarization of the Lu 5\textit{d} states through the Ho\textsubscript{1−\textit{x}}Lu\textsubscript{\textit{x}}(Fe\textsubscript{1−\textit{y}}Al\textsubscript{\textit{y}})\textsubscript{2} series has been studied by means of X-ray magnetic circular dichroism. The combined study of the dichroic signals performed at the Fe K-, Ho L\textsubscript{2} and Lu L\textsubscript{2,3}-edges gives a complete picture of the polarization scheme at the conduction band. The results point out that in the presence of competing localized magnetic moments, $\mu_{\text{Fe}}$ and $\mu_{\text{Ho}}$, the dichroic signal at the Lu site is mainly due to the Fe atoms, being negligible the effect of the magnetic rare-earth. Estimation of the spin and orbital components of the Lu(5\textit{d}) induced magnetic moment have been obtained by applying the magneto-optical sum rules derived for X-ray magnetic circular dichroism.

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

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1. Introduction

The magnetic polarization of non-magnetic atoms, plays an important role into determining the magnetic properties of many systems [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. However, the exact nature of the induced magnetic moments remains an open problem, whose clarification is a key step for the understanding of the magnetic interactions in these systems. This is the case of the rare-earth 5d states in rare-earth – transition metal (R-T) intermetallics which mediate the R-T interaction via de R(5d)-T(3d) hybridization [13, 14, 15].

Previous works have demonstrated that, in R-T intermetallics, these R(5d) states can be explored not only by means of XMCD measurements at the R L\textsubscript{2,3}-edges, but also by measuring at the T K-edge [16, 17, 18, 19, 20, 21, 22, 23, 24]. It has been shown that the dichroic spectra at the T K- and R L\textsubscript{2,3}-edges are a simultaneous fingerprint of the magnetism of both transition-metal and rare-earth, even when only one atomic element is probed. More specifically, in these systems the transition metal contributes to the rare-earth L\textsubscript{2,3}-edges XMCD, spectra and, conversely, there is a contribution of the lanthanide metal to the XMCD recorded at the K-edge of the transition metal [16, 17, 18, 19, 20, 21, 22, 23, 24]. The proper disentanglement of these crossed contributions, XMCD\textsubscript{R} at the Fe K- and XMCD\textsubscript{Fe} at the R L\textsubscript{2}-edges, provides selective magnetic information from the study of the dichroic signals at the conduction band [25, 26, 27]. So far, these dichroic signals have been studied for magnetic absorbing atoms in which either 4f or 3d localized magnetic moments were present. However, little is known about both the magnetic polarization and the XMCD behaviour of non-magnetic atoms as Lu in the presence of localized magnetic moments.

In this work, we have faced the problem of determining which localized magnetic moment, R(4f) and/or Fe(3d), is responsible for the induced magnetic polarization of the Lu 5d states. To this end, we have synthesized two series, Ho\textsubscript{1-x}Lu\textsubscript{x}Fe\textsubscript{2} and Ho\textsubscript{0.5}Lu\textsubscript{0.5}(Fe\textsubscript{1-y}Al\textsubscript{y})\textsubscript{2}, in which the relative contribution of both 4f and 3d moments is controlled. In the former case, for a fixed Fe contribution, the magnetization of the rare-earth sublattice is progressively depleted by increasing the Lu content. Therefore, the polarization of the Lu 5d states due to the Fe 3d ones is maintained fixed, while that of the Ho 4f states decreases. Whereas in the latter series, the polarization of the Lu 5d states due to Ho atoms is fixed, while the polarization due to Fe atoms decreases by increasing the concentration of non-magnetic Al.

Therefore we have studied how the modification of the magnetization of each magnetic sublattice as well as the R-Fe hybridization affect the magnetic polarization of the Lu 5d states by recording the XMCD at the Lu L\textsubscript{2,3}-edges. Our results point out that in the presence of competing localized magnetic moments, μ\textsubscript{Fe}(3d) and μ\textsubscript{Ho}(4f), the dichroic signal at the Lu site is mainly due to the Fe atoms, being negligible the effect of the magnetic rare-earth.
2. Experimental

Ho_{1-x}Lu_xFe_2 (x = 0, 0.25, 0.5, 0.75, 1) and Ho_{0.5}Lu_{0.5}(Fe_{1-y}Al_y)_2 (y = 0, 0.25, 0.5, 0.75, 1) series were prepared by arc-melting the pure elements under Ar protective atmosphere. The ingots were annealed at 850 °C for one week. X-ray diffraction (XRD) patterns were recorded to determine the crystallographic structure and the degree of crystallinity of all the synthesized samples. Measurements have been performed on powdered samples at room temperature by using a Cu Kα radiation in Bragg-Brentano geometry, 2θ = 15 – 80° (Rigaku RTO 500RC diffractometer). Magnetization measurements, M(H), were performed at T = 5 K by using a commercial superconducting quantum interference device magnetometer (Quantum Design MPMS-5S).

XMCD experiments were performed at the beamline BL39XU of the SPring-8 facility [28]. XMCD spectra were recorded in the transmission mode at the Fe K- and at the rare-earths L_{2,3}-edges by using the helicity-modulation technique [29]. Circularly polarized X-rays were generated using a diamond phase plate 0.73 mm-thick. For the measurements, homogeneous layers of the powdered samples were made by spreading fine powders of the material on adhesive Kapton tape. The 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 room temperature under the action of a H = 50 kOe magnetic field.

The dichroic signal was obtained as the difference of the absorption coefficient \( \mu_c = \mu^- - \mu^+ \) for antiparallel \( \mu^- \) and parallel \( \mu^+ \) orientation of the photon helicity and sample magnetization. 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. In all 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

3.1. Structural and magnetic characterization

Figure 1 shows the evolution of the XRD patterns through the Ho_{1-x}Lu_xFe_2 and Ho_{0.5}Lu_{0.5}(Fe_{1-y}Al_y)_2 series. X-ray diffraction characterization indicates that all the samples show a single C15 Laves phase, with the exception of Ho_{0.5}Lu_{0.5}(Fe_{0.5}Al_{0.5})_2 which shows the C14 structure as expected for intermediate Fe concentrations [30]. The patterns of the compounds with C15 structure are nearly identical and only a small shift upon dilution is found. This shift is due to the modification of the crystal cell parameters: lattice expansion (contraction) occurs upon replacing Fe by Al (Ho by Lu) leading to a displacement of the peaks towards lower (higher) 2θ angle.

The structural information derived form the Rietveld refinement is summarized in
Competing effects in the magnetic polarization of non-magnetic atoms.

Table 1. Structural information derived from Rietveld refinement of XRD patterns: crystal structure, lattice parameter (± 0.5 × 10⁻³), reliability Bragg factor associated to the main phase and percentage of secondary phases (see text for details).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structure</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>R_{Bragg}</th>
<th>Secondary Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HoFe₂</td>
<td>C15</td>
<td>7.294</td>
<td>-</td>
<td>9.44</td>
<td>&lt;2% R₂O₃</td>
</tr>
<tr>
<td>Ho₀.₇₅Lu₀.₂₅Fe₂</td>
<td>C15</td>
<td>7.278</td>
<td>-</td>
<td>9.83</td>
<td>&lt;1% RFe₃</td>
</tr>
<tr>
<td>Ho₀.₅Lu₀.₅Fe₂</td>
<td>C15</td>
<td>7.254</td>
<td>-</td>
<td>10.5</td>
<td>&lt;1% R₂O₃</td>
</tr>
<tr>
<td>Ho₀.₂₅Lu₀.₇₅Fe₂</td>
<td>C15</td>
<td>7.241</td>
<td>-</td>
<td>9.78</td>
<td>&lt;1% R₂O₃</td>
</tr>
<tr>
<td>LuFe₂</td>
<td>C15</td>
<td>7.217</td>
<td>-</td>
<td>7.51</td>
<td>&lt;2% R₂O₃</td>
</tr>
<tr>
<td>Ho₀.₅Lu₀.₅(Fe₀.₇₅Al₀.₂₅)₂</td>
<td>C15</td>
<td>7.372</td>
<td>-</td>
<td>7.83</td>
<td>&lt;2% R₂O₃</td>
</tr>
<tr>
<td>Ho₀.₅Lu₀.₅(Fe₀.₅Al₀.₅)₂</td>
<td>C14</td>
<td>5.320</td>
<td>8.658</td>
<td>1.04</td>
<td>&lt;2% R₂O₃</td>
</tr>
<tr>
<td>Ho₀.₅Lu₀.₅(Fe₀.₂₅Al₀.₇₅)₂</td>
<td>C15</td>
<td>7.657</td>
<td>-</td>
<td>10.1</td>
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</tr>
<tr>
<td>Ho₀.₅Lu₀.₅Al₂</td>
<td>C15</td>
<td>7.773</td>
<td>-</td>
<td>10.5</td>
<td>&lt;4% RAl₃ + &lt;2% R₂O₃</td>
</tr>
</tbody>
</table>

table 1: crystal structure, lattice parameters and the reliability Bragg factor associated to the main phase. Good crystallinity of the samples is indicated by the low Bragg factors obtained. In all the cases, as indicated in table 1, the presence of secondary phases has been proved to be almost negligible.

Figure 2(a) shows the magnetic field dependence of the magnetization recorded at T = 5 K for Ho₁₋ₓLuₓFe₂ series. In all cases, the magnetization is nearly saturated at H ≳ 10 kOe. Hence, the saturation magnetization will be taken as the magnetization measured at T = 5 K and H = 50 kOe.

In the Ho₁₋ₓLuₓFe₂ compounds the Fe magnetic moments are collinear and anti-
ferromagnetically coupled to those of Ho, resulting in a ferrimagnetic behaviour. This ferromagnetic coupling can lead to a reversal in the dominant magnetic sublattice in the case of Ho$_{1-x}$Lu$_x$Fe$_2$ compounds, which has to be taken into account when analysing the XMCD data.

The magnetization measured at T = 5 K and H = 50 kOe Ho$_{1-x}$Lu$_x$Fe$_2$ can be accounted for by applying a two sublattice model. Within this approach, the total magnetization, $M_{\text{Tot}}$, corresponds to the simple addition of the magnetization of both magnetic sublattices: $M_{\text{Tot}} = M_{\text{Ho}} + M_{\text{Fe}}$ and, therefore, the direction of the total magnetization of the system stems from the competition of the two magnetic sublattices. In this way, the absolute value of the total magnetization of the diluted Ho$_{1-x}$Lu$_x$Fe$_2$ compounds can be expressed as: $|M_{\text{Tot}}| = |(1-x)\mu_R - 2\mu_{\text{Fe}}|$. In the two sublattice model, it is usually assumed that $M_{\text{Fe}}$ corresponds to the magnetization of the RFe$_2$ compounds in which R is non-magnetic, LuFe$_2$, that is $\mu_{\text{Fe}} \approx 1.41 \mu_B$ [31]. Similarly, $\mu_{\text{Ho}}$ is taken as the magnetization value of the Ho$_{0.5}$Lu$_{0.5}$Al$_2$ compounds measured at the same experimental conditions ($\mu_{\text{Ho}} \sim 9.25 \mu_B$). This procedure reproduces well the values of the magnetization measured at T = 5 K and H = 50 kOe. It is important to remark that there is a critical concentration of the non-magnetic rare-earth, $x_c \sim 0.7$, for which the total magnetization of the system becomes zero at T = 5 K. Consequently, for concentrations below $x_c$, the magnetization of the rare-earth sublattice dominates over the Fe one and it determines the direction of the total magnetization of the system, whereas the contrary holds for $x > x_c$.

The $M(H)$ curves recorded at T = 5 K on the Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$ compounds are displayed in figure 2(b). In this case, since the Lu content is always lower than $x_c$ for all the members of the Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$ series, the Ho magnetic sublattice always dominates the direction of the total magnetization. The saturation magnetization

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Isothermal magnetization curves measured at T = 5 K for (a) Ho$_{1-x}$Lu$_x$Fe$_2$: x = 0 (black, ◼), 0.25 (red, ●), 0.5 (green, ▲), 0.75 (blue, □) and 1 (cyan, ♦); and (b) Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$: y = 0 (green, ▲), 0.25 (magenta, ◼), 0.5 (black, ■), 0.75 (orange, ●) and 1 (dark yellow, solid line).}
\end{figure}
increases when Fe is progressively diluted by Al due to the antiferromagnetic coupling between Fe and Ho magnetic sublattices. In contrast to the behaviour found for the Ho\textsubscript{1−x}Lu\textsubscript{x}Fe\textsubscript{2}, the saturation magnetization through the Ho\textsubscript{0.5}Lu\textsubscript{0.5}(Fe\textsubscript{1−y}Al\textsubscript{y})\textsubscript{2} series does not follow a linear variation, as it would be expected from a simple dilution effect [31]. These magnetization measurements confirm the results obtained from X-ray absorption spectroscopy (XAS) studies performed on the Ho\textsubscript{1−x}Lu\textsubscript{x}(Fe\textsubscript{1−y}Al\textsubscript{y})\textsubscript{2} series. The substitution of the rare-earth by Lu acts as a simple magnetic dilution effect whereas the Fe-Al substitution leads to a decrease of the R(5d)-Fe(3d) hybridization and induces magnetic disorder into the Fe sublattice [32, 33].

3.2. XMCD measurements

To get a deeper insight into the origin of these two different magnetic trends we will study how the polarization of the conduction band states changes through the Ho\textsubscript{1−x}Lu\textsubscript{x}(Fe\textsubscript{1−y}Al\textsubscript{y})\textsubscript{2} series depending on which magnetic atom, Ho or Fe, is substituted. As a first step, we will determine if the behaviour observed in the magnetization and XAS measurements is also reflected in the XMCD signals recorded at the Fe K- and Ho L\textsubscript{2}-edges. Additionally, studying the variation of the XMCD signal at Lu L\textsubscript{2,3}-edges will be crucial to discern which magnetic atom mainly determines the magnetic polarization of the Lu 5d states.

**Fe K-edge and Ho L\textsubscript{2}-edge**

Figure 3 shows the Fe K- and Ho L\textsubscript{2}-edge XMCD signals through the Ho\textsubscript{1−x}Lu\textsubscript{x}(Fe\textsubscript{1−y}Al\textsubscript{y})\textsubscript{2} series recorded at T = 5 K and H = 50 kOe. In panels (a) and (d), the dichroic signals have been displayed with the sign obtained from the experimental measurements. As commented above, LuFe\textsubscript{2} and Ho\textsubscript{0.25}Lu\textsubscript{0.75}Fe\textsubscript{2}, x > x\textsubscript{c}, undergo a change of the dominant magnetic sublattice and, accordingly, the characteristic features of the dichroic signal have opposite sign than the rest of the compounds [27]. In order to be able to discern the evolution of the different dichroic contributions, the XMCD spectra has been referred to the direction of the magnetization of the Ho sublattice in the rest of the panels of figure 3, i.e., the sign of the dichroic signals for x = 0.75 and 1 has been reversed.

The Fe K-edge spectra are composed by two different magnetic contributions, the Fe one, XMCD\textsubscript{Fe}, is more intense close to the absorption threshold (peak A) while the contribution due to the magnetic rare-earth, XMCD\textsubscript{Ho}, extends over a wider energy range and dominates the shape of the XMCD spectra (peaks B, C\textsubscript{1}, C\textsubscript{2} and D), see figure 3(b) and (c).

In the case of the Ho\textsubscript{1−x}Lu\textsubscript{x}Fe\textsubscript{2}, see figure 3(b), i.e., when only Ho is substituted by Lu, both the shape and the energy position of the main spectral features remain unvaried. However, the amplitude of the peaks associated to XMCD\textsubscript{Ho} (B, C\textsubscript{1}, C\textsubscript{2} and D) decreases as the Lu content increases. The uniformly decrease of these XMCD\textsubscript{Ho}
Figure 3. XMCD spectra at the Fe K- [panels (a), (b) and (c)] and at the Ho L$_2$-edges [panels (d), (e) and (f)] for Ho$_{1-x}$Lu$_x$(Fe$_{1-y}$Al$_y$)$_2$ series recorded at T = 5 K and H = 50 kOe. Upper panels (a) and (d) display the dichroic signals with their signs obtained experimentally and shifted for clarity. Dichroic signals of Ho$_{1-x}$Lu$_x$Fe$_2$ are displayed in the panels (a), (b), (d) and (e): x = 0 (black, ▽), 0.25 (red, ☆), 0.5 (green, ▲), 0.75 (blue, □) and 1 (cyan, ♦); and Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$ ones in the lower panels: y = 0 (green, ▲), 0.25 (magenta, ○), 0.5 (black, ■), 0.75 (orange, ●) and 1 (dark yellow, solid line). Insets in panels (e) and (f) shows the XMCD$_{Fe}$ contribution extracted from the Ho L$_2$-edge XMCD spectra of Ho$_{1-x}$Lu$_x$Fe$_2$ and Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$, respectively. See text for details.

features with the Ho concentration indicates that the substitution of Ho by Lu acts as a simple magnetic dilution effect.
By contrast, the substitution of Fe by Al, see figure 3(c), affects the shape, energy position and amplitude of the XMCD spectra. More specifically, the increase of the Al content diminishes the intensity of the main dichroic features ($B, C_1, C_2$ and $D$) which shift towards lower energy.

It has been previously determined that the magnetic moment remains close to its free-ion value through the Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$ series [16]. Consequently, the observed reduction of the XMCD$_{Ho}$ contribution to the Fe K-edge is in agreement with previous findings reporting a progressive reduction of the R-Fe exchange induced by the Al substitution through the reduction of the Ho(5$d$)-Fe(3$d$) hybridization [32].

The results obtained at the Fe K-edge are confirmed by the XMCD measurements performed at the Ho L$_2$-edge through the Ho$_{1-x}$Lu$_x$(Fe$_{1-y}$Al$_y$)$_2$ series.

Ho L$_2$-edge XMCD spectra recorded at $T = 5$ K and $H = 50$ kOe through both series are shown in panels (d)-(f) of figure 3. In the case of compounds without Fe, Ho$_{0.5}$Lu$_{0.5}$Al$_2$, the dichroic signal is composed by a main negative peak $A$ and a positive one $B$ at higher energies. As the amount of Fe increases, the intensity of peak $A$ decreases and, in several cases a weak positive peak $A_1$ arises. This $A_1$ peak is associated to the Fe contribution at the Ho L$_2$-edge XMCD. Indeed, its intensity remains constant through the Ho$_{1-x}$Lu$_x$Fe$_2$, i.e., when the Fe content is maintained fixed, while it decreases through the Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$ as the Fe content does. By contrast, the intensity of peak $B$ does not vary with the Fe content but with the Ho one, which demonstrates that this peak is mainly due to the Ho contribution.

The influence of the Fe sublattice in the Ho L$_2$-edge XMCD spectra can be evaluated by extracting the XMCD$_{Fe}$ contribution. To this end we have subtracted the dichroic signal of Ho$_{0.5}$Lu$_{0.5}$Al$_2$, i.e., of a homologous compound which does not contain Fe, from the Ho L$_2$-edge XMCD spectra through the series. The results indicate that the XMCD$_{Fe}$ extracted from the Ho$_{1-x}$Lu$_x$Fe$_2$ spectra almost does not vary through the series. In fact, the intensity of the main peak matches for all the Ho$_{1-x}$Lu$_x$Fe$_2$ compounds, see inset of figure 3(e). By contrast, the intensity of the XMCD$_{Fe}$ signal decreases through the Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$ series upon substitution of Fe by Al [see inset of figure 3(f)]. This amplitude reduction cannot only be accounted for in terms of the dilution of the Fe sublattice since it does not vary linearly with the Fe content (as it will be shown in the inset of figure 5(b)). Indeed, the substitution of Fe by Al induces magnetic disorder in the 3$d$ magnetic sublattice as well as the modification of the electronic structure, as confirmed by magnetization and XAS measurements [32, 33]. Consequently, the observed decrease of the XMCD$_{Fe}$ contribution can be ascribed to the reduction of the Ho(5$d$)-Fe(3$d$) hybridization associated with the modification of the magnetic properties of the 3$d$ magnetic sublattice.

**Lu L$_{2,3}$-edges**

So far we have shown that the dilution of the Fe and Ho magnetic sublattices affects differently the XMCD spectra recorded at both Fe K- and Ho L$_2$-edges. In
b) d) 

Figure 4. Lu L$_{2,3}$-edges XMCD signals measured at T = 5 K and H = 50 kOe for Ho$_{1-x}$Lu$_x$Fe$_2$ series: 0.25 (red, ⋄), 0.5 (green, ▲), 0.75 (blue, □) and 1 (cyan, ♦). Upper panels (a) and (c) display the dichroic signals with their signs obtained experimentally and shifted for clarity. Inset in panel (b) displays the intensity difference of peaks B, D and F respect to the LuFe$_2$ signal. See text for details.

brief, the Ho-Lu substitution through the Ho$_{1-x}$Lu$_x$Fe$_2$ series acts as a simple magnetic dilution and does not modify the Ho(5d)-Fe(3d) hybridization. By contrast, the Fe-Al substitution through the Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$ series yields the depletion of the Ho(5d)-Fe(3d) hybridization and induces disorder into the Fe magnetic sublattice. Now, we will apply the previous results to the study of the magnetic polarization of the Lu 5d states. Our aim is to determine which magnetic species, Ho or Fe, is responsible for the appearance of a magnetic moment at the Lu sites.

To this end, we have performed a Lu L$_{2,3}$-edges XMCD study of the Ho$_{1-x}$Lu$_x$(Fe$_{1-y}$Al$_y$)$_2$ series. Figure 4 shows the Lu L$_{2,3}$-edges XMCD spectra of the Ho$_{1-x}$Lu$_x$Fe$_2$ series recorded at T = 5 K and H = 50 kOe. Panels (a) and (c) display the dichroic signals with the sign obtained from the experimental measurements and shifted vertically for clarity. Panels (b) and (d) the sign of the compounds with x = 0.75 and 1 has been reversed for better comparison. The Lu L$_3$-edge dichroic signal, see figure 4(b), is composed by a main negative peak A located at E-E$_0$ ~ 1 eV and a less intense positive peak B at ~ 10 eV. The shape and intensity of the spectral feature A exhibit subtle
Competing effects in the magnetic polarization of non-magnetic atoms.

Figure 5. Lu L_{2,3}-edges XMCD signals measured at T = 5 K and H = 50 kOe for Ho_{0.5}Lu_{0.5}(Fe_{1−x}Al_x)2 series: y = 0 (green, ▲), 0.25 (magenta, ⌂), 0.5 (black, ■), 0.75 (orange, ●) and 1 (dark yellow, solid line). Inset in panel (a) is an enlarged view of peak B. Inset in panel (b) compared the intensity of XMCD signal of peaks A and C with that of XMCD_{Fe} at the Ho L_{2}-edge. See text for details.

Figure 6. Comparison of the Lu L_{2,3}-edges XMCD spectra for Ho_{0.5}Lu_{0.5}(Fe_{0.25}Al_{0.75})_2 (orange, ●) and Ho_{0.5}Lu_{0.5}Al_2 (dark yellow, line) at T = 5 K and H = 50 kOe.

changes through the series, whereas the intensity of peak B decreases upon increasing the Lu content up to almost vanishing for LuFe_2. In the case of the Lu L_{2}-edge XMCD spectra, see figure 4(d), the dichroic signal is composed by a main peak C located at E-E_0 ∼ 0 eV and two other less intense peaks, D and F, located at E-E_0 ∼ 4 eV and ∼ 7 eV, respectively. Peak C remains nearly unvaried upon dilution of the Ho sublattice whereas the intensity of both D and F peaks markedly decreases upon increasing the Lu content. In other words, the shape of the XMCD spectra at both Lu L_{2,3}-edges is mostly retained upon substitution of Ho by Lu and only minor changes are observed at both edges through the Ho_{1−x}Lu_xFe_2 series. Since the Fe content is kept constant through the Ho_{1−x}Lu_xFe_2 series and only the Ho content is varied, this suggest that the magnetic polarization at the Lu sites is mainly due to the Fe magnetic moments.
On the other hand, the intensity of the less intense peaks B (Lu L$_3$-edge), D and F (Lu L$_2$-edge) varies upon increasing the Lu content. The intensity difference respect to the LuFe$_2$ dichroic spectrum, see inset in figure 4(b), shows a linear decrease as the Ho content decreases which indicates that the intensity of these peaks is proportional to the Ho concentration. Therefore, this observation confirms that the effect of the magnetic polarization of the Lu 5$d$ states due to the Ho atoms is clearly smaller than that due to the Fe ones.

Similar comparisons performed on the Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$ series are shown in figure 5. The Lu L$_3$-edge XMCD spectrum is composed by a main negative peak A and a less intense peak B. In the present case, the intensity of the main peak A decreases notably as the Al content increases. The intensity of peak B is clearly less affected by the substitution and only a slight narrowing together with a shift to lower energies is observed. Similar results are found in the Lu L$_2$-edge XMCD spectra [see panel (b) of figure 5]. The main peak C decreases and the peaks above the absorption edge, D and F, are less affected.

The observed reduction of the intensity of the main peaks A and C at the Lu L$_3$- and L$_2$-edge, respectively, indicates that the Fe polarization of the Lu 5$d$ states is dramatically affected by the Al substitution. As shown in the inset of figure 5(b), the amplitude of the main dichroic peak at both Lu L$_{2,3}$-edges follows the same dependence with the Fe content, a trend which also coincides with that of the XMCD$_{Fe}$ contribution at the Ho L$_2$-edge. Contrary to the case of the Ho-Lu substitution, this reduction does not scale with the Fe content. Moreover, the evolution of the dichroic signal when Al concentration increases suggest that for compounds with Al concentration equal or higher than 75% the Fe contribution has almost vanished. Indeed, as it is clearly shown in the enlarged view displayed in figure 6, the Lu L$_{2,3}$-edges XMCD spectrum of Ho$_{0.5}$Lu$_{0.5}$(Fe$_{0.25}$Al$_{0.75}$)$_2$ overlap with that of Ho$_{0.5}$Lu$_{0.5}$Al$_2$, which does not contain Fe. This implies that the magnetic polarization by the Fe atoms becomes negligible for compounds with low Fe concentration and only the polarization due to the Ho ones remains, which is clearly less intense. These results confirm our previous findings regarding the electronic impact of the Fe-Al substitution that cannot be regarded as a simple dilution effect in the 3$d$ magnetic sublattice.

Further confirmation that the Fe sublattice is mainly responsible for the magnetic polarization of the Lu 5$d$ states instead of the rare-earth one can be obtained by studying the temperature dependence of the Lu L$_{2,3}$-edges XMCD signals. In these compounds, the magnetization of the Fe sublattice undergoes a decrease of $\sim$7% from T = 5 K to ambient while the R magnetization is markedly reduced, around 50%, in the same temperature range. Accordingly, if Fe sublattice is mainly responsible for the magnetic polarization of the Lu 5$d$ states, the intensity of the XMCD spectra should not vary appreciably between T = 5 K and room temperature. By contrast, if this polarization is mainly due to the Ho sublattice this intensity should be strongly depressed at high temperature.

By this reason, we have recorded the Lu L$_{2,3}$-edges XMCD spectra of Ho$_{1-x}$Lu$_x$Fe$_2$
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Figure 7. Comparison of Lu L$_3$- (a) and L$_2$-edges (b) XMCD signals at $T = 5$ K (dotted black line) and 288 K (solid red line) for Ho$_{0.75}$Lu$_{0.25}$Fe$_2$ and Ho$_{0.25}$Lu$_{0.75}$Fe$_2$. Dichroic spectra for each different compound have been shifted for clarity and those of the $x = 0.75$ have been displayed with the sign reversed for sake of comparison.

at $T = 288$ K. The comparison displayed in figure 7 shows that the amplitude of the XMCD spectra remain nearly unvaried and only a slight decrease is observed when the temperature increases. A detailed analysis of the evolution of the dichroic features yields that upon warming, from $T = 5$ K to 288 K, the intensity of the main peaks exhibits a decrease of $\sim 7.5\%$ which is in agreement with the decreasing of the magnetization of the Fe sublattice. By contrast, the relative variation of the intensity of the less intense peaks, associated to the Ho sublattice (see above), is about $\sim 76\%$, in agreement with the variation of the Ho sublattice magnetization. Thus, these results confirm that the appearance of a magnetic polarization at the Lu sites in the Ho$_{1-x}$Lu$_x$(Fe$_{1-y}$Al$_y$)$_2$ series is mainly due to the Fe magnetic moments.

Finally, we have obtained a quantitative determination of the magnetic moment of Lu through the studied series by applying the so-called XMCD sum rules [34, 35] to the Lu L$_{2,3}$-edges XMCD spectra. These sum rules have been derived by connecting the integrated XMCD spectra at the Lu L$_{2,3}$-edges with the ground-state expectation value of both $\langle L_z \rangle$ and $\langle S_z \rangle$ of the 5$d$ states [36]:

$$\langle L_z \rangle = 2 (A_{L_3} + A_{L_2}) \frac{n_h}{\mu},$$

$$\langle S_z \rangle + \frac{7}{2} \langle T_z \rangle = \frac{3}{2} (A_{L_3} - 2A_{L_2}) \frac{n_h}{\mu},$$

where $A_{L_3}$ and $A_{L_2}$ are the integrals over the dichroic signal at the L$_3$ and L$_2$ edges respectively, $n_h$ is the number of holes in the Lu(5$d$) band, $\langle T_z \rangle$ is expected value of the $z$ component of the magnetic dipole operator and $\mu$ is the unpolarized L$_{2,3}$-edges cross
Competing effects in the magnetic polarization of non-magnetic atoms.

Figure 8. LuFe$_2$ Lu L$_{2,3}$-edges XAS (black, solid line) and XMCD (green, ●) and the respective integrated curves. (see text for details).

The analysis of the XMCD signals has been performed under the following assumptions: i) $\mu$ is approximated by $\frac{3}{2}(\mu^+ + \mu^-)$; ii) $\langle T_z \rangle$ is assumed to be negligible in the spin sum rule; iii) estimates of both the orbital and spin moments, $\mu_{\text{orb}} = -\langle L_z \rangle \mu_B$ and $\mu_{\text{spin}} = -2\langle S_z \rangle \mu_B$ respectively, have been derived from the sum-rule by considering $n_h = 9$. It is well known that the sum rules cannot be applied to account for the L$_{2,3}$-edge XMCD spectra of those lanthanides showing a localized (4$f$) magnetic moment. However, in the case of La and Lu it has been largely demonstrated that the sign of the XMCD is the ”right” one as there is no breathing effect. In this way the sum rules are commonly applied to determine the magnetic moment (of 5$d$ origin) of Lu [36, 38].

Figure 9 shows the results obtained after applying the sum rules procedure. For sake of comparison the magnetic moments have been displayed with their absolute value. In the case of Ho$_{1-x}$Lu$_x$Fe$_2$ series, the magnetic moment of Lu, mainly of spin character (see table 2), does not vary appreciably whereas it decreases abruptly through the Ho$_{0.5}$Lu$_{0.5}$(Fe$_{1-y}$Al$_y$)$_2$ when the aluminum content increases. The decrease of the Lu magnetic polarization upon Fe substitution is in agreement with the previous discussion regarding the intensity variation of the dichroic signals. This confirms that the magnetic polarization at the Lu site is mainly due to the Fe atoms and that, in addition, not only the Fe content but also both the hybridization and the magnetic disorder affect the value of the magnetic moment induced at the Lu site.
Figure 9. Orbital (blue, ○), spin (red, ■) and total (black, ★) magnetic moments of the Lu 5d states for Ho1−xLuxFe2 and Ho0.5Lu0.5(Fe1−yAl)y2 derived from the sum rules procedure. For sake of comparison absolute values of the values displayed in table 2 have been represented.

Table 2. Orbital and spin magnetic moments (in μB) of the Lu 5d states derived from the XMCD sum-rules analysis at T = 5 K. The uncertainty of these values is estimated to be of 15 %.

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<thead>
<tr>
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<th>μ_orb</th>
<th>μ_spin</th>
<th>μ_Lu(5d)</th>
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<td></td>
<td></td>
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<td>0.118</td>
<td>0.116</td>
</tr>
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<td>-0.111</td>
</tr>
<tr>
<td>Ho0.5Lu0.5(Fe1−yAl)y2</td>
<td></td>
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</tr>
<tr>
<td>y = 0</td>
<td>-0.005</td>
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4. Summary and Conclusions

Summarizing, we have presented here a systematic XMCD measurement on Ho1−xLuxFe1−yAly2 series to study the Lu 5d states magnetic polarization in the presence of competing polarizations, Fe and Ho localized magnetic moments. The analysis of the Fe K- and Ho L2-edge XMCD spectra have proved that the substitution of
Fe by Al leads to a depletion of the Ho(5d)-Fe(3d) hybridization and induces magnetic disorder in the Fe sublattice, whereas the dilution of Ho by Lu behaves as a simple magnetic dilution. The evolution of the Lu L2,3-edges XMCD spectra through the Ho1-xLu2x(Fe1-yAl_y)2 series shows that the magnetic polarization at the Lu site is constant through the Ho1-xLu2Fe2 series and decreases upon increasing the Al content through Ho0.5Lu0.5(Fe1-yAl_y)2. This demonstrates that the appearance of a magnetic moment at the Lu sites is mainly due to the Fe magnetic moments. Estimation of the spin and orbital components of the Lu(5d) induced magnetic moment have confirmed these results and that the magnetic moment of Lu is mainly of spin character.

Acknowledgments

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