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Rare-Earth-Transition-Metal Intermetallics: Experimental
Probe of the Rare-Earth Magnetic Moment**

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X-ray magnetic circular dichroism at the iron K edge in rare-earth-transition-metal intermetallics: Experimental probe of the rare-earth magnetic moment

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We present a systematic x-ray magnetic-circular-dichroism (XMCD) study performed at the Fe K edge on the $R_2\text{Fe}_{14}\text{B}$ series (R =rare earth and Y). The magnetic XMCD signal has been identified as due to the addition of two components associated with the magnetic contributions from the iron and the rare-earth sublattices. The contribution of the rare-earth sublattice has been extracted from the total XMCD signal. The integrated XMCD signal of the R component is proven to be directly correlated with the R magnetic moment. [S0163-1829(97)50202-5]

Since the discovery of $\text{Nd}_2\text{Fe}_{14}\text{B}$,¹ worldwide efforts have been conducted to find novel materials among the iron-rich ternary compounds based on rare earths (R) showing high hard-magnet performance. Moreover, the interstitial doping with light elements such as hydrogen or nitrogen has been profusely developed as to become a new route to improve the permanent-magnet technological performance of previously well-known R -Fe compounds.

Previous x-ray absorption spectroscopy investigations have addressed the existence of strong electronic effects induced upon light atoms charging.² They conclude that the interplay between electronic charge transfer to the conduction bands and the change of the $R(5d)$ - $\text{Fe}(3d)$ hybridization play a major role in governing the modification of the electronic and magnetic properties of these systems. According to Campbell's model, the R -Fe interaction is determined by the $5d$ - $3d$ hybridization through intra-atomic $4f$ - $5d$ exchange interactions and direct interatomic $3d$ - $5d$ spin-spin interactions, so that the R and Fe magnetic moments are ferromagnetically (antiferromagnetically) coupled for light (heavy) rare earths.³ Therefore, it is of paramount interest to characterize magnetically the $R(5d)$ states, which tune the magnetic properties of the R -Fe intermetallic compounds, to obtain a further verification of these results.

This information can be gained by means of the x-ray magnetic-circular-dichroism (XMCD) technique. Indeed, one of the most striking capabilities of XMCD applied to R -Fe intermetallics lies in the possibility of directly probing

the spin polarization of the $5d$ empty states of the rare-earth $L_{2,3}$ edges. Moreover, it offers, in principle, the capability to separate the spin and orbital contributions to the magnetic moments by use of theoretical sum rules derived within an atomic framework.⁴ This model is able to describe also in a rather satisfactory way the XMCD signal coming from localized electronic states [$\text{Fe}(3d)$ $L_{2,3}$ edges, $R(4f)$ $M_{4,5}$ edges]. However, recent works have shown the limitations of these sum rules,⁵ so that their validity when applied to $L_{2,3}$ -edge spectra of rare-earth metals is strongly questioned. In addition, Wang *et al.* have shown that the conventional two-step description of the XMCD process fails to account for the R $L_{2,3}$ -edge spectra because it neglects the spin dependence of the transition matrix elements induced by the $5d$ - $4f$ exchange.⁶ Indeed, systematic studies of the spin-dependent $L_{2,3}$ absorption in R -Fe intermetallics indicate that the sign of the $L_{2,3}$ XMCD signals cannot be directly correlated to the mutual orientation of the rare-earth and iron magnetic moments.^{7,8} In the case of the iron K edge, where the $4p$ empty states of Fe are probed, the interpretation of the XMCD spectra is still far from being solved. The K -Fe XMCD profile has been described by taking into account the spin splitting of the final p -projected states at the Fe site and the hybridization of the $4p$ and $3d$ states⁹ so that in some cases the behavior of the XMCD amplitude has been shown to be correlated to variations in the local magnetization.^{9,10} However, to date the relationship between the Fe K -edge XMCD signals and the local magnetic moments is not well-defined.

In this paper we report a systematic Fe *K*-edge XMCD study at the *K* edge on $R_2\text{Fe}_{14}\text{B}$ systems. Our results show that the study of the Fe *K*-edge XMCD signal yields an experimental way to overcome the limitations of the $L_{2,3}$ -edge analysis to characterize the *R* 5*d*-states. Our study shows how the Fe *K*-edge XMCD signal is due to the addition of magnetic contributions from both the iron and the rare-earth sublattices, so that they can be isolated and correlated to the iron and rare-earth magnetic moments.

XMCD experiments have been performed at the iron *K* edge in $R_2\text{Fe}_{14}\text{B}$ ($R=\text{Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, Ho, Tm, Yb, and Lu}$). Several polycrystalline samples were measured in different experimental runs at the Photon Factory (PF) synchrotron radiation facility of the National Laboratory for High Energy Physics (KEK) in Tsukuba. The magnetic XMCD experiments were performed at room temperature in the transmission mode using left circularly polarized x rays on beamline 28*B* at PF-KEK. The PF storage ring was operated with a positron beam energy of 2.5 GeV and a maximum stored current of 360 mA. The x-ray radiation was monochromatized using a Si(220) double-crystal monochromator, being the degree of circular polarization after monochromatization $P_c \sim 0.35$.¹¹ The XMCD spectra were recorded by reversing the sample magnetization for a fixed polarization of the incoming radiation. In our experimental setup a magnetic field of 0.6 T was applied parallel to the plane of the sample at 45° to the incident beam and reversed twice for each energy value.

The spin-dependent absorption coefficient has been 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. The spectra were normalized to the averaged absorption coefficient at high energy, μ_0 , in order to eliminate the dependence of the absorption on the sample thickness, so that $\mu_c(E)/\mu_0 = [\mu^-(E) - \mu^+(E)]/\mu_0$ corresponds to the dimensionless spin-dependent absorption coefficient. The origin of the energy scale was chosen at the inflection point of the absorption edge.

In Fig. 1 we show the normalized Fe *K*-edge XMCD signals for the measured $R_2\text{Fe}_{14}\text{B}$ compounds. In the case of the nonmagnetic rare earths (La, Ce) and Y, the XMCD spectra exhibit a characteristic two-peak structure at the absorption edge, similar to that of pure iron. The positive peak is very narrow, of about 4 eV, whereas the negative dip at higher energy covers an energy width of about 12 eV. In the case of the light rare-earth compounds ($R=\text{Pr, Nd, and Sm}$), the XMCD signals exhibit a strong modification with respect to the nonmagnetic *R* based compounds: (i) the negative dip gets narrower (~ 8.5 eV) and its intensity becomes ~ 2.5 times higher; (ii) an additional positive (~ 8 eV wide) contribution arises at the high-energy side of the negative dip. This behavior is not exhibited by the heavy rare-earth compounds: the XMCD signal of $\text{Gd}_2\text{Fe}_{14}\text{B}$ resembles that of Fe metal or $R_2\text{Fe}_{14}\text{B}$ compounds in which *R* is a nonmagnetic rare earth, see Fig. 1, except for a small positive contribution arising just in the center of the negative dip. The intensity of this feature is found to increase across the series from Gd to Ho, for which the maximum intensity is reached, followed by a progressive decrease till near disappearance for Yb. For $\text{Lu}_2\text{Fe}_{14}\text{B}$ the normal behavior for nonmagnetic *R* is re-

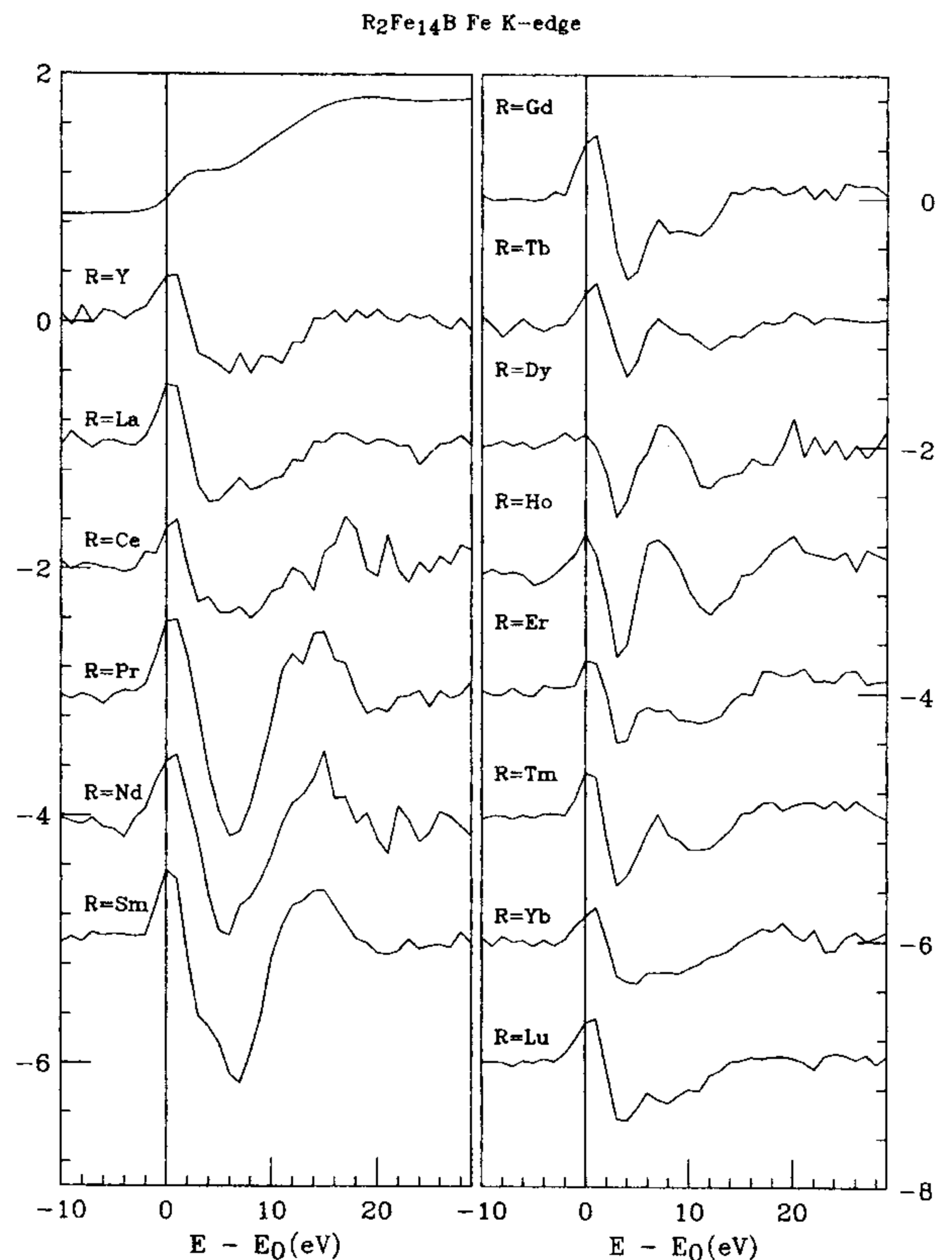


FIG. 1. Normalized x-ray magnetic circular dichroism spectra at the Fe *K*-edge for the $R_2\text{Fe}_{14}\text{B}$ compounds ($R=\text{rare earth and Y}$). The scale ($\times 10^3$) is referred to the $R=\text{Y}$ (left panel) and $R=\text{Gd}$ (right panel) case. For sake of clarity, the normalized Fe *K*-edge XAS spectrum for $\text{Y}_2\text{Fe}_{14}\text{B}$ is also shown.

gained. This result is an indication of the influence of the particular rare-earth magnetic atom on the *K*-Fe XMCD profile of each compound. The observed experimental behavior across the series indicates that this influence strongly depends on the magnetic state of the rare earth, i.e., nonmagnetic *R*, light *R* ($\mathbf{J}=\mathbf{L}-\mathbf{S}$ coupling), and heavy *R* ($\mathbf{J}=\mathbf{L}+\mathbf{S}$ coupling).

In order to obtain a deeper insight on the origin of such behavior we have performed a further analysis in the framework of a two-magnetic sublattice model. In this model, it is assumed that: (i) the total magnetization of the $R_2\text{Fe}_{14}\text{B}$ compounds is the addition of the magnetization of the iron and the rare-earth sublattices, i.e., $M_T = M_R + M_{\text{Fe}}$; and (ii) the contribution of the Fe sublattice to the magnetization, M_{Fe} , is identical to that of $\text{Y}_2\text{Fe}_{14}\text{B}$. For each compound in the lanthanide series, the subtraction of this contribution to the magnetization allows one to sort out the magnetic contribution coming from the rare-earth sublattice. In identical manner, in our model we assume the hypothesis that the total Fe *K*-edge XMCD signal results from the addition of two components, associated with the magnetic contribution from the Fe and *R* sublattices, respectively. To analyze our data under this model, we have subtracted first the Fe *K*-edge XMCD signal of $\text{Y}_2\text{Fe}_{14}\text{B}$ from the Fe *K*-edge XMCD spectra of the $R_2\text{Fe}_{14}\text{B}$ series as shown in Fig. 2, then, the remaining signal in the XMCD spectra is assigned to the rare-earth sublattice magnetic contribution. The validity of such an assumption is supported by the fact that in the case of the

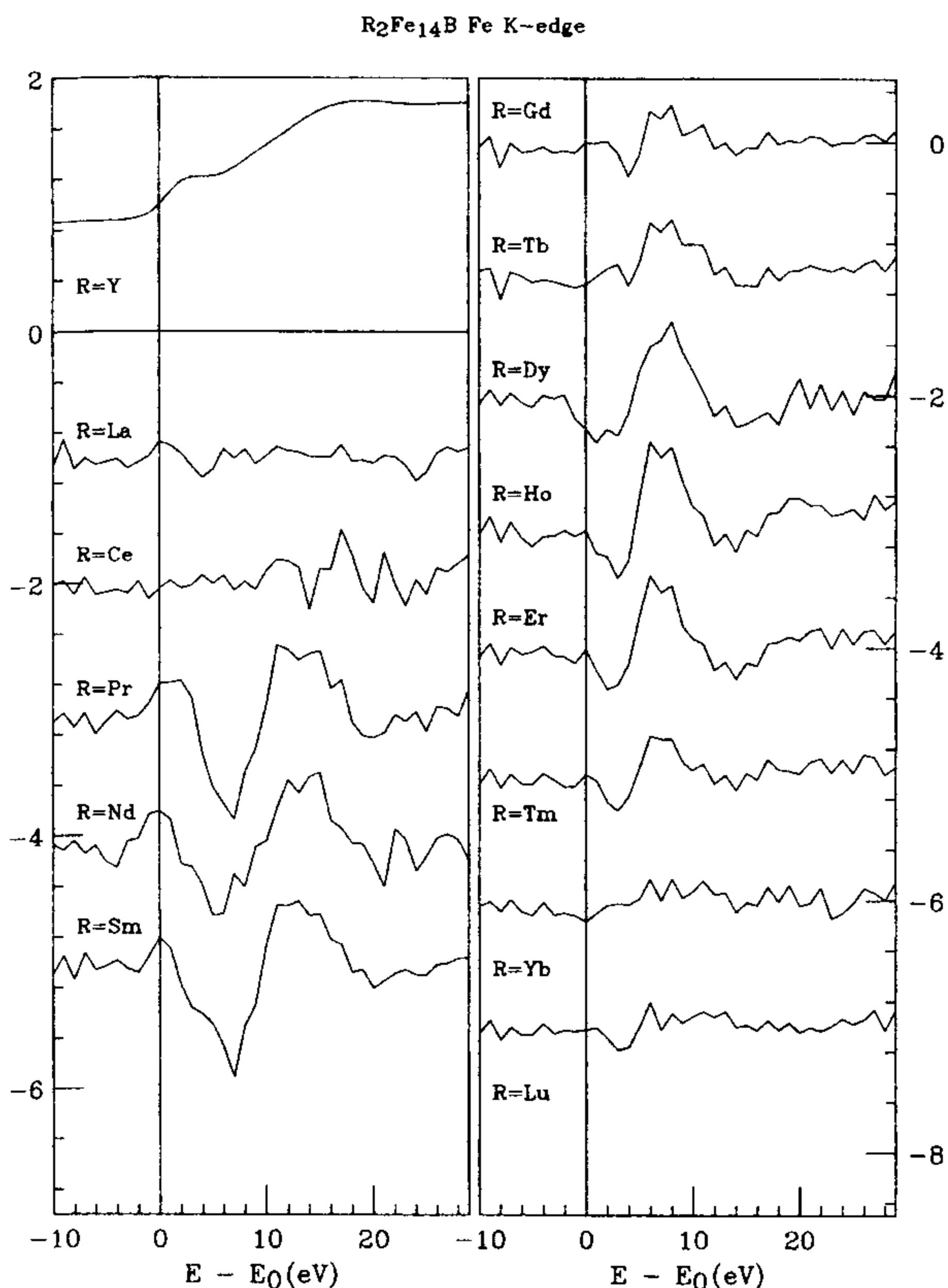


FIG. 2. Normalized x-ray magnetic circular dichroism spectra at the Fe K -edge for the $R_2\text{Fe}_{14}\text{B}$ compounds (R =rare earth and Y), after the subtraction of the $\text{Y}_2\text{Fe}_{14}\text{B}$ XMCD signal. The scale ($\times 10^3$) is referred to the $R=\text{Y}$ (left panel) and $R=\text{Gd}$ (right panel) case. For sake of clarity, the normalized Fe K -edge XAS spectrum for $\text{Y}_2\text{Fe}_{14}\text{B}$ is also shown.

nonmagnetic R -based compounds, (La, Ce, and Lu), the signals obtained by subtraction of the $\text{Y}_2\text{Fe}_{14}\text{B}$ signal are zero within the signal-to-noise ratio, i.e., the Fe $4p$ moment is nearly constant in the series. Indeed, despite that under substitution of yttrium by a magnetic lanthanide the mean magnetic contribution of iron to the magnetization is increased up to 8%, Mössbauer effect measurements on ^{57}Fe in $R_2\text{Fe}_{14}\text{B}$ compounds suggest that the electronic configuration of iron atoms is nearly the same for all these compounds, and that the iron $3d$ shell dominates the contribution due to the conduction electron polarization to the Fe hyperfine fields.¹²

After applying the subtraction procedure the remaining signal for all the investigated light- R compounds ($R=\text{Pr}$, Nd , and Sm) exhibits a negative peak centered at (~ 7 eV) above E_0 with a width that ranges between 6.5 and 9 eV, and a positive peak at ~ 13 eV above the edge, its width ranging between 7.4 and 8.2 eV. In the case of the heavy rare-earths compounds the negative peak is strongly depressed, the main feature on the signal being a positive peak located at about 7 eV above the edge, with a width that varies from 5.7 to 7 eV across the series.

Within a one-electron framework and by introducing the difference of the density of empty states, $\Delta(E)$, the XMCD at the Fe K edge is proportional to $\Delta\rho(E) = \rho^\downarrow(E) - \rho^\uparrow(E)$, where \downarrow (\uparrow) holds for the majority (minority) spin density.^{13,14} In the case of iron metal, the XMCD profile has

been accounted for by considering the spin splitting of the final p -projected states at the Fe site and the hybridization of the $4p$ and $3d$ states, which modulates the weight of the spin-dependent absorption cross-section for transitions towards majority (minority) $4p$ states.¹⁴ In the $R_2\text{Fe}_{14}\text{B}$ compounds, the Fe sublattice ($3d^\downarrow$, majority) determines the sign of the magnetization. In the R -Fe intermetallic compounds a strong hybridization between the rare earth $5d$ and Fe- $3d$ orbitals is present, so one can expect an additional influence of the R magnetic state on the Fe K -edge XMCD signal. The subtraction of the $\text{Y}_2\text{Fe}_{14}\text{B}$ contribution from the total $R_2\text{Fe}_{14}\text{B}$ Fe K -edge XMCD signal, (Fig. 2), would lead to isolation of the R contribution to the Fe K -edge XMCD.

In this way, the two-peak profile of the R contribution found in the case of the light- R compounds (see Fig. 2) can be associated with the exchange splitting of the $5d$ bands which occurs when there is a nonzero $4f$ moment at the R site, because of the intra-atomic $4f$ - $5d$ overlap. This raises the energy of the R -minority $5d$ band of the R sublattice with respect to that of its majority band. Hence, the negative sign of the XMCD signal indicates that the spin of the $5d$ band just above the Fermi level is antiparallel ($5d^\uparrow$) to that of the Fe atoms ($3d^\downarrow$). So, the experimental XMCD signal identifies the dominant $5d$ levels close to the Fermi level as those of the minority-spin band, while the change of sign in the R contribution to the XMCD signal for increasing energy implies that above a certain energy the density of $5d$ -majority band becomes dominant. This result is in agreement with previous electronic structure calculations showing that the highly localized $4f$ peak is found to be located near the Fermi level, and that the center of the $5d^\downarrow$ ($5d^\uparrow$) band is located at about 4.7 (6.7) eV above E_F .¹⁵ On the other hand, when a heavy- R (Gd) is involved, the occupied $4f$ level lies below the Fermi level and the empty $4f$ orbitals lies at about 3.1 eV above the Fermi level.¹⁶ The XMCD data, showing a prominent positive peak only indicating that the dominant $5d$ empty states correspond to the majority $5d$ band, are in agreement to these electronic calculations.

The above results indicate unambiguously that the extracted contribution to the Fe K -edge XMCD signal shown in Fig. 2 reflects the magnetic state of the R atoms in these systems. In a simple model we propose that the Fe K -edge XMCD signals are directly related to the Fe($4p,3d$)- R ($5d$) hybridized band, and that the extracted signals resemble the magnetic state of the rare earth through the splitting of the $5d$ component due to the exchange interaction with the $4f$ magnetic moments. If so, the extracted signals should be related to the magnitude of the R magnetic moments. To verify this point we present in Fig. 3 the comparison between the rare-earth $4f$ magnetic moments according to Russell-Saunders coupling and the absolute value of Fe K -edge integrated XMCD signal for the $R_2\text{Fe}_{14}\text{B}$ compounds after subtracting the $\text{Y}_2\text{Fe}_{14}\text{B}$ spectrum. The maximum integrated XMCD signal, corresponding to the Dy-based compound, has been scaled to the Dy magnetic moment, and the proportionality factor found was then applied to the whole XMCD signals. The remarkable proportionality between the integrated R -component signal and g_J supports the above hypothesis and thus the validity of our model of additive contributions to the XMCD. Moreover, the R -component integrated signal changes sign from the light- R compounds (negative) to the heavy- R compounds (positive). This result agrees with the

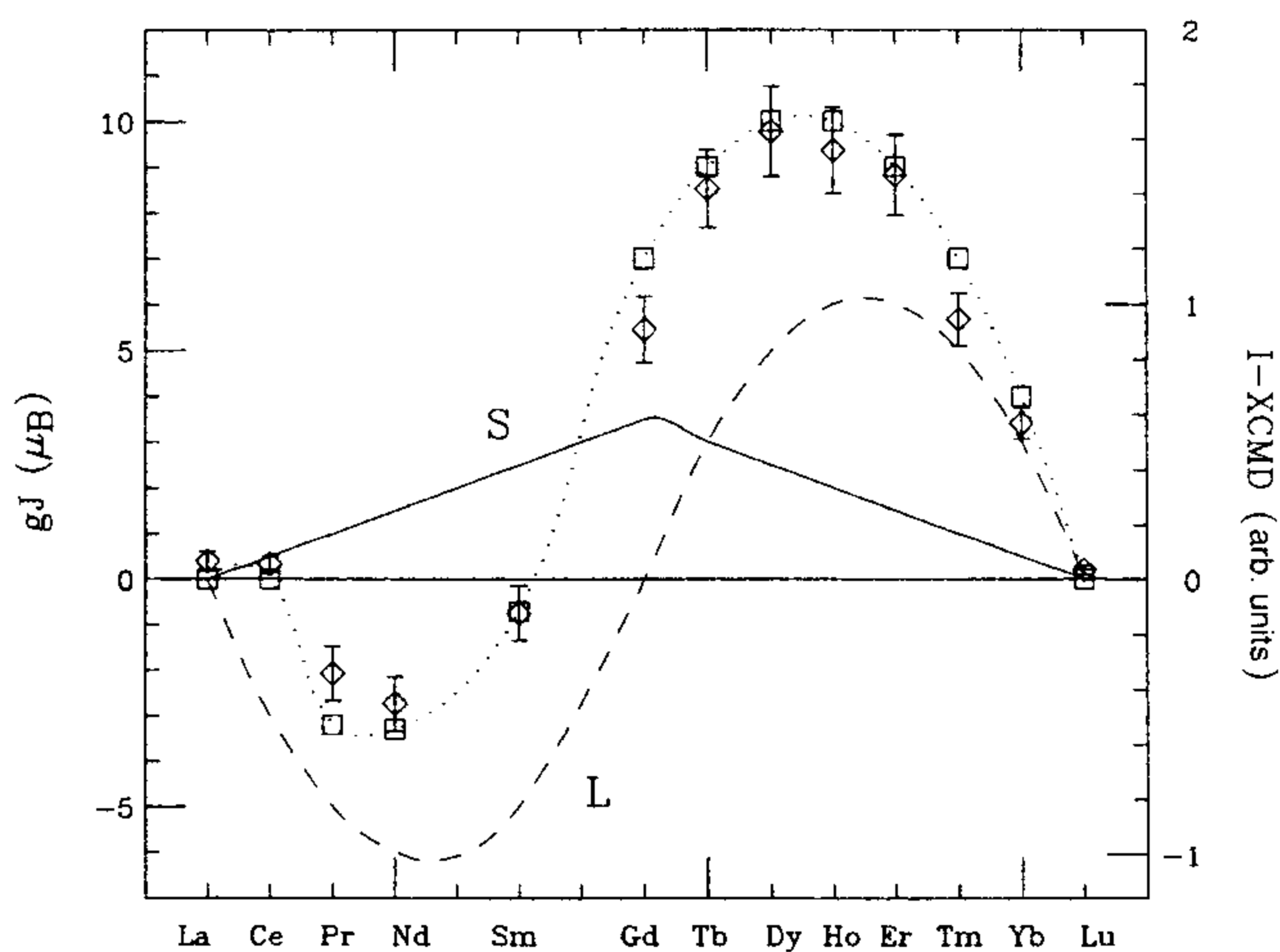


FIG. 3. Comparison between the rare-earth $4f$ magnetic moments, gJ , according to Russell-Saunders coupling (\square) and the Fe K -edge integrated XMCD signal for the $R_2\text{Fe}_{14}\text{B}$ compounds, (\diamond), after subtracting the $\text{Y}_2\text{Fe}_{14}\text{B}$ spectrum (see text for details). The values of S (solid line) and L (dashed line) for the ground state of rare-earth ions along the lanthanide series are also shown, where the sign refers to the spin of the Fe atoms, according to Campbell's model (Ref. 3).

known fact that the R and Fe magnetic moments are parallel(antiparallel) in the light- R (heavy- R) R -Fe intermetallic compounds. We conclude that the extracted signal reflects both the direction and magnitude of the rare-earth magnetic

moment. This result is rather surprising in view of the expected dependence of the R - M interaction on the $5d$ spin value, according to the current models for $R(4f-5d)$ spin-spin coupling.¹⁷ Our results point towards the existence of non-negligible orbital contribution of the $5d$ magnetic moment, arising from the overlap of the $5d$ and $4f$ shells, that is in agreement with the model proposed by Jo and Imada to account for the electron distribution in the $5d$ state due to the $4f-5d$ exchange interaction.¹⁸ A similar conclusion has been reached from the correlation found between the branching ratio of the XMCD effect at $L_{2,3}$ edges and the orbital angular momentum of the rare earth (L_z^{4f}) in $R\text{Fe}_2$ Laves phases.¹⁹

Our study identifies the influence of the rare-earth magnetic state into the Fe K -edge XMCD signals in $R_2\text{Fe}_{14}\text{B}$ intermetallic compounds. This signal results from the addition of two components, each one being due to the magnetic contribution of both the iron and the rare-earth sublattices. The contribution of the R sublattice to the XMCD signal has been extracted yielding a direct correlation to the R magnetic moment. Therefore we provide an approach to characterize magnetically the $R(5d)$ states and thus, the R -Fe interaction, in R -Fe intermetallics materials.

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