X-ray magnetic circular dichroism at the rare earth $L_{2,3}$ edges in $R_2Fe_{14}B$ intermetallics

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We present a systematic x-ray magnetic circular dichroism (XMCD) study performed at the rare-earth (R) $L_{2,3}$ edges on the $R_2Fe_{14}B$ series. The identification of multipolar contributions to the signal allows the application of sum rules to the obtained XMCD spectra. The results show that both orbital and spinorial components of the R(5d) magnetic moment are proportional to the 4f ones. Hence, the magnetic moment of 5d shell derived from a sum-rules analysis evidences an important nonquenched orbital contribution. This result is in contradiction with Campbell's model for R–Fe intermetallic compounds. Consequently, both XMCD sum rules and Campbell's model have to be revised in the atomic level. [S0021-8979(00)50408-3]

In 1972 Campbell proposed a phenomenological model to account for the magnetic coupling of the magnetic moments in R–Fe intermetallic compounds.[1] In these systems there is an antiferromagnetic coupling between Fe spin and R(4f) spins. For compounds in which R is a light rare-earth element (J=L−S) this implies that the total rare-earth moment (gJ) is coupled parallel to the Fe moments. By contrast, when R is a heavy rare-earth element (J=L+S) the total rare-earth moment is coupled antiparallel coupled to the Fe moment. The Campbell's hypothesis suggests an indirect exchange interaction in which the f electron spin of the rare-earth creates a positive local d moment through the ordinary $f-d$ exchange and that there are then direct $d-d$ interactions with any other d moment as in normal transition metals. The basic idea behind the model is that treating rare earth as transition elements they are all at the beginning of the transition series for which interactions between d moments on rare-earth sites will be ferromagnetic.

This model is consistent with existing magnetic data and consequently commonly adopted when studying R–Fe intermetallics. More recently, Brooks and co-workers have tried to give a theoretical ground to it by means of local spin density electronic structure and self-consistent energy band calculations.[2] Both of them underline the critical role of the rare-earth 5d electrons in the propagation of interaction between the R(4f) and Fe(3d) magnetic moments via the $4f-5d$ and the $5d-3d$ spin–spin interactions. Therefore, it is of paramount interest to determine the origin and the exact nature of the $3d-5d$ interaction, what implies to magnetically characterize the R(5d) states. However, this is a hard task because the response of these 5d conduction electrons is small and then hindered masked by the R(4f) and Fe(3d) magnetic signals.

In recent years the advent of an x-ray magnetic circular dichroism (XMCD) technique has attracted great interest in the study of R–Fe intermetallics as it provides a direct probe of the spin polarization of the 5d empty states of the rare earth. 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.[3] The possibility of applying XMCD to obtain information about these states has stimulated extensive series of XMCD at the $L_{2,3}$ edges of rare-earth compounds.[4,5] However, no experimental report has been published showing the result of the sum-rules application to the rare-earth $L_{2,3}$ edges. The reason for it may reside in that their interpretation is a matter of debate. In particular, one of the main problems concerns the understanding of the features present in the R–$L_{2,3}$ XMCD spectra as they can be of dipolar or quadrupolar origin. Identification of quadrupolar features in the dichroic spectra is essential in correctly applying the sum rules because dipolar and quadrupolar transitions obey distinct sum rules.[6,7]

In this work we present a detailed study of the XMCD at the rare-earth L_2 and L_3 edges in the $R_2Fe_{14}B$ series. Taking advantage of a recent resonant inelastic x-ray scattering (RIXS) experiment performed on the same samples,[8] it has been possible to separate the dipolar and quadrupolar contributions to the XMCD signals and thus to correctly apply the sum rules in order to determine the orbital and spinorial components of the R(5d) magnetic moment through the $R_2Fe_{14}B$ series.

XMCD experiments have been performed at the R $L_{2,3}$ edges in $R_2Fe_{14}B$ compounds (R=La, Pr, Nd, Sm, Gd, Tb, Dy, Er, Ho, Tm, Yb, and Lu). Several polycrystalline samples were measured in different experimental runs on beamline 28B at the Photon Factory in Tsukuba. The XMCD spectra were recorded at room temperature in the transmission mode by reversing the sample magnetization for a fixed polarization of the incoming radiation. The sample was mounted with the incident plane tilted 45° away from the beam direction and a magnetic field of 0.6 T was applied parallel to the plane of the sample and reversed twice for each energy value.

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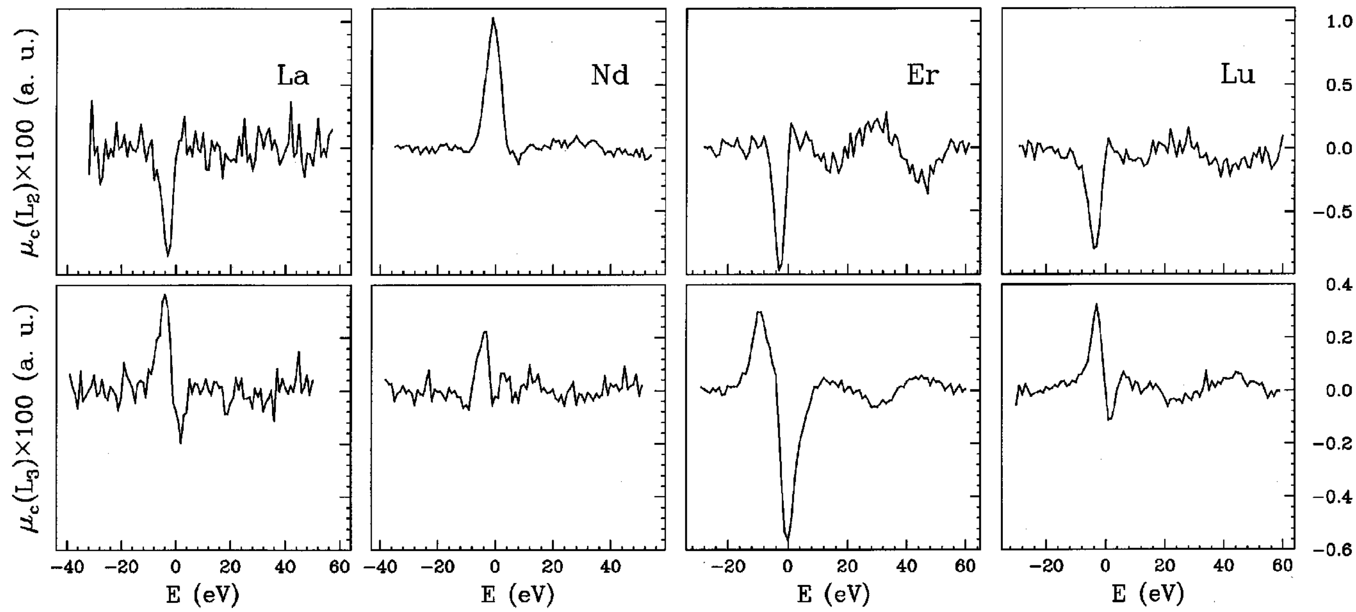

FIG. 1. Normalized XMCD spectra at the rare-earth L_2 (top) and L_3 (bottom) edges for selected $R_2Fe_{14}B$ compounds. For sake of simplification the Nd–L_2 and Er–L_3 have been plotted using a 50% reduction factor to maintain a unique scale.

Selected XMCD spectra recorded at the rare-earth L_2 and L_3 edges in the $R_2Fe_{14}B$ series are shown in Fig. 1 (the complete set of data can be found in Ref. 5). In the case of L_2 absorption, the XMCD signal is dominated for a single peak that change its sign depending on the magnetic character of the rare earth: it is negative for nonmagnetic R (La, Ce, and Lu); positive for light rare earths (Pr, Nd, and Sm) and negative for heavy rare earths (Er, Tm, and Yb). For Gd and Tb the signal is positive, contrary to the rest of the heavy rare earths, an effect that has been discussed in terms of breathing effects.[9] The only exceptions to this single-peak shape are Dy and Ho that show two lobules, the first (low-energy) positive and the second negative, i.e., it seems that the signal evolves from the positive sign of Tb to negative of Er. In other words, there is a competition between the weakening of the breathing effect as we progress through the heavy rare-earth $4f$ subshell. On the contrary, the shape of the XMCD signals at the R–L_3 edge is more complicated as there are different contributions of different sign what is due to the presence of quadrupolar contributions to the XMCD being more intense at the L_3 than at the L_2 edge.

Being our final aim to correctly apply the sum rules to these $L_{2,3}$ dichroic spectra we have to extract this quadrupolar contribution as dipolar and quadrupolar transitions obey distinct sum rules.[6,7] Then, we have performed the deconvolution of the XMCD spectra into their dipolar and quadrupolar contributions taking advantage of a RIXS experiment performed on the same samples.[8] The deconvolution has been performed by fitting the dichroic spectra by a combination of pseudovoigt profiles centered at the quadrupolar and main dipolar resonant incident energies determined by RIXS plus some *ad hoc* included profiles to give account of the higher energy XMCD oscillations.[7]

Trying to obtain a deeper insight on the magnitude of μ_{5d}(R) in the series, we have applied the sum rules to the XMCD spectra (corrected for the rate of circular polarization).[3] Initially, we have applied these rules to the XMCD spectra without correcting them from quadrupolar transitions. Moreover, we have considered that T_z is vanishingly small in the same way as the $3d$ electrons because in principle the $5d$ electrons are well delocalized. The dispersion of the found values is very high. However, it should be noted that there is a clear change of sign from light to heavy rare earths in $5d$-$\langle L_z \rangle$, while $5d$-$\langle S_z \rangle$ is always negative. We have refined the sum-rule application by removing the quadrupolar contributions as described earlier. The results

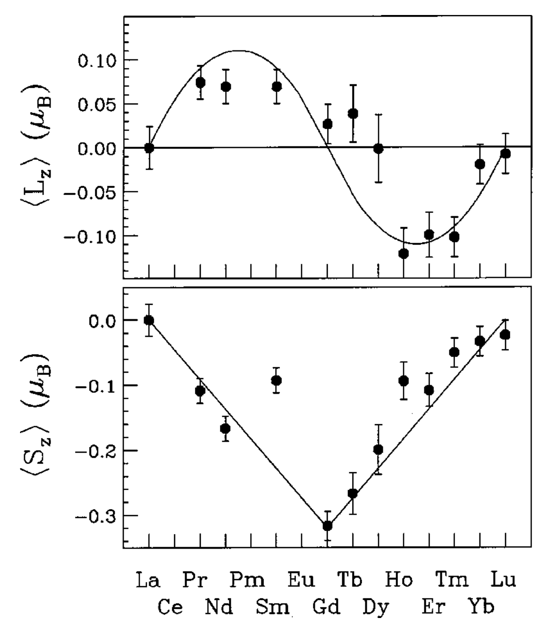

FIG. 2. Rare-earth $5d$ $\langle L_z \rangle$ and $\langle S_z \rangle$ values derived from the experimental R–$L_{2,3}$-edges XMCD signals of the $R_2Fe_{14}B$ compounds by applying the sum rules after substraction of the quadrupolar contributions. The solid line corresponds to the scaled variation of L and S for the ground state of rare-earth ions according to Russel–Saunders coupling.

are shown in Fig. 2 and compared to the scaled variation of L and S for the ground state of rare-earth ions according to Russel–Saunders coupling. The proportionality between the L and S values for rare-earth $4f$ and $5d$ electrons through the $R_2Fe_{14}B$ series is remarkable. It should be noted that the discrepancy in $5d$-$\langle L_z\rangle$ for Gd, Tb, and Dy can be accounted as due to the breathing effect,[9] while that of $\langle S_z\rangle$ in Sm is in agreement to the mixture of the ground state and the first excited state in the multiplet.

The earlier results indicate that both orbital and spinorial components of the R($5d$) magnetic moment are proportional to the $4f$ ones. In particular, the magnetic moment of $5d$ shell derived from a sum-rules analysis evidences an important nonquenched orbital contribution. This result implies that the Campbell's model for R–Fe intermetallic compounds have to be revised in the atomic level, as the magnetic interaction between the R($4f$) and Fe($3d$) magnetic moments is assumed to be of pure spin character for both $4f$–$5d$ and $5d$–$3d$ interactions. The question posed by these results extends also to the reliability of the information derived from a sum-rule analysis of XMCD data. Indeed, the applicability of the sum rules to the rare-earth $L_{2,3}$ is a matter of current study, as it seems that the presence of the $4f$ unfilled shell and the $4f$–$5d$ exchange implies that the shape of the XMCD spectra is essentially driven by $4f$ electrons.[10,11] However, it should be noted that Thole *et al.* already considered this problem when deriving the orbital sum rule,[3] showing that the presence of an extra (partly filled) shell has no effect on the integrated XMCD although it may change the shape of the spectrum. Consequently, our results pushed out to a strong revision of both XMCD sum rules, as also suggested by Natoli,[11] and Campbell's model for the magnetic coupling in R–Fe intermetallics.

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