

Modification of the rare-earth magnetic moment upon hydrogen absorption in R -Fe intermetallics probed by Fe K -edge x-ray magnetic circular dichroism

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(Received 14 July 1997; revised manuscript received 30 January 1998)

We present a systematic x-ray magnetic circular dichroism (XMCD) study performed at the Fe K edge on the hydride derivatives of several R -Fe intermetallic materials (R =rare earth and Y). The XMCD signal is identified as being rare-earth dependent. The analysis of the dichroic signal has been performed according with a two-sublattice model making a parallel to standard magnetization procedure. The contribution of the rare-earth sublattice to the total Fe K -edge XMCD signal has been extracted and proven to be directly correlated to the R magnetic moment, which is determined to decrease upon hydrogen absorption.

[S0163-1829(98)02821-5]

Most of the intermetallic compounds formed among rare earths (R) and elements of the d -transition series (M) can form stable hydrides and, very often, hydrogen absorption leads to strong changes of the macroscopic structural and magnetic properties of these materials.¹ The interest in the study of these hydrides has been triggered in the last years by the discovery of the $R_2\text{Fe}_{14}\text{B}$ materials.^{2,3} Notwithstanding that these $R_2\text{Fe}_{14}\text{B}$ compounds exhibit high-performance permanent-magnet properties, their ordering temperatures T_c are sufficiently low to render them unsuitable for some technological applications.⁴ Consequently, a great body of research has been devoted to overcome this limitation, being found that hydrogen absorption is one of the most notable mechanisms able to achieve higher magnetic ordering temperature in these systems.^{5,6}

For all the $R_2\text{Fe}_{14}\text{B}$ compounds an increase of the magnetization and T_c was found upon hydrogen uptake.¹ The increase in the magnetization is usually ascribed to the enhancement of the Fe magnetic moments, in agreement with the increase of the hyperfine field at the different Fe sites measured by ^{57}Fe Mössbauer spectroscopy.⁷ The Fe moment enhancement is usually deduced from the analysis of magnetization data by considering that the R moments do not change after the hydrogen loading. Indeed, despite the fact that the moment increase indicates that hydrogen exerts an appreciable influence on the electronic structure of the system, it is a common practice to consider the R moments as being less sensitive to the hydrogen uptake. However, hydrogen atoms are located in the vicinity of the R atoms and a dramatic loss in the magnetocrystalline anisotropy, dominated by the rare-earth contribution, is observed upon

hydrogenation.⁸ Therefore it seems reasonable to consider that the rare-earth sublattice should also be affected by the absorption process. Dalmas de Reotier *et al.* have proposed that the overlap of the Fe $3d$ and R $5d$ wave functions may be screened by hydrogen and thus increase the localization and magnitude of the Fe moments.⁹ This proposition is in agreement with rare-earth nuclei Mössbauer spectroscopy and x-ray absorption spectroscopy results, reporting, respectively, the significant reduction of the hyperfine fields, directly related to the R magnetic moment, and the modification of the $R(5d)$ -Fe($3d$) hybridization upon hydrogen uptake.¹⁰⁻¹² This $3d$ - $5d$ hybridization is the key role into governing the R -Fe interaction and, consequently, the magnetic properties of the system. Therefore, it is of paramount interest to characterize magnetically the conduction states to obtain a deeper insight into the mechanism which tunes the change of the magnetic properties of the $R_2\text{Fe}_{14}\text{B}$ intermetallics upon hydrogen uptake.

In this work we present a detailed x-ray magnetic circular dichroism (XMCD) study performed at the Fe K edge in the $R_2\text{Fe}_{14}\text{BH}_x$ hydrides, in order to obtain a better understanding of the role played by hydrogen into driving the modification of the magnetic behavior of these intermetallic compounds. XMCD experiments have been performed at the iron K edge in the $R_2\text{Fe}_{14}\text{BH}_x$ hydrides, where x , the maximum hydrogen content, ranges from 3.5 to 6 as a function of the rare earth (R =Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Ho, and Lu).^{6,14} Samples were prepared by arc melting the starting elements (purity 99.9%) under purified Ar atmosphere. Both phase and structural analysis were performed on a standard x-ray diffractometer. The hydrogen absorption-desorption

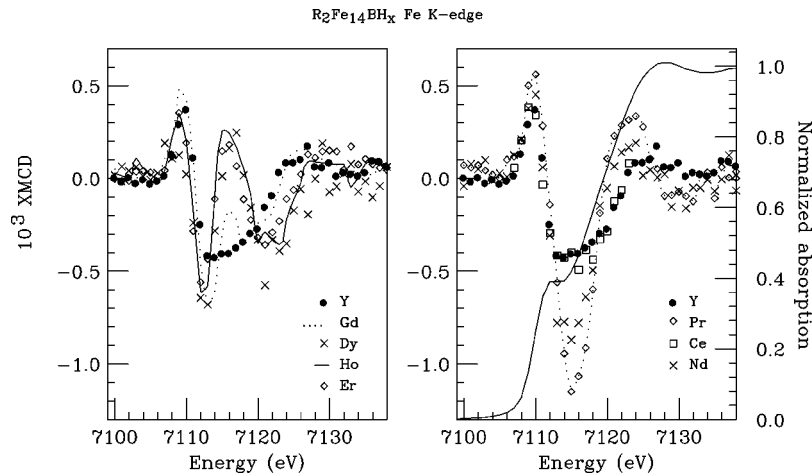


FIG. 1. Normalized x-ray magnetic circular dichroism spectra at the Fe K edge for the $R_2\text{Fe}_{14}\text{BH}_x$ compounds. Left panel: $R=\text{Y}$ (circles), Gd (dots), Dy (crosses), Ho (solid line), and Er (open triangles). Right panel: $R=\text{Y}$ (circles), Ce (open squares), Nd (crosses), and Pr (open diamonds). For sake of clarity, the normalized Fe K -edge XAS spectrum for $\text{Y}_2\text{Fe}_{14}\text{BH}_x$ is also shown in the right panel (solid line).

properties were established according to the standard methods,^{6,14} by using a volumetric automated experimental setup described elsewhere.¹⁵

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 28B 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, with the degree of circular polarization after monochromatization being $P_c \sim 0.35$.¹⁶ 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 normalized Fe K -edge XMCD signals obtained in this way for the $R_2\text{Fe}_{14}\text{B}$ hydrides are shown in Fig. 1. In the case of compounds in which R is nonmagnetic, Y, La, Ce, and Lu, the shape of the XMCD signal is closely related to that of Fe metal.¹³ The spectra shows a narrow positive peak at the absorption threshold, ~ 4 eV wide, followed by a broad negative dip, ~ 12 eV wide. No significant differences, other than slight intensity changes, are detected in the comparison of the XMCD spectra for the Y-, La-, and Ce-based hydrides. On the contrary, the XMCD signals corresponding to magnetic rare-earth based compounds show a dramatic change with respect to those of the nonmagnetic R -based

compounds. This is illustrated in Fig. 1, where the Fe K -edge XMCD signal of $\text{Y}_2\text{Fe}_{14}\text{BH}_x$ is compared to that of the $R_2\text{Fe}_{14}\text{BH}_x$ compounds with $R=\text{Ce}$, Nd, Pr, Gd, Dy, Ho, and Er.

In the case of compounds in which R is a light rare earth, no modification of the positive peak shape is detected, and only its intensity is slightly modified with respect to the nonmagnetic R -based compounds case. However, the negative dip appears to be very sensitive to the rare-earth substitution. Indeed, in the case of $\text{Pr}_2\text{Fe}_{14}\text{BH}_x$ and $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$ compounds, the original negative dip of the XMCD signal splits into two peaks of different sign. The low-energy part of this feature is negative and ~ 7.7 eV wide, and becomes positive as energy increases giving rise to a well defined positive peak ~ 6.2 eV wide. Moreover, the intensity of the negative part of the new structure is considerably higher, at least twice as high as that of the negative peak of the Fe K -edge XMCD signal of the hydrides in which the rare earth is nonmagnetic (see Fig. 1).

In the case of the $R_2\text{Fe}_{14}\text{BH}_x$ compounds involving heavy rare earths, i.e., Gd, Dy, Ho, and Er, the shape of the XMCD signals, specially the negative dip, differs from that exhibited by the nonmagnetic R compounds. As shown in Fig. 1, the whole XMCD spectra of both $\text{Y}_2\text{Fe}_{14}\text{BH}_x$ and $\text{Gd}_2\text{Fe}_{14}\text{BH}_x$ compounds are very similar, resembling that of pure Fe. However, in the case of Gd, there is a small positive contribution arising just in the center of the negative dip, that is detected neither for the nonmagnetic Y-, La-, and Ce-based, nor for the light rare-earth-based compounds. This positive feature grows through the heavy rare-earth series to become dominant in the case of Ho over the negative dip, as shown in Fig. 1. Moreover, in the case of $\text{Ho}_2\text{Fe}_{14}\text{BH}_x$ the shape of the XMCD signal beyond this positive structure is modulated up to form a second negative structure in the high-energy part of the spectra. As a consequence, if the XMCD signals of $\text{Pr}_2\text{Fe}_{14}\text{BH}_x$ and $\text{Ho}_2\text{Fe}_{14}\text{BH}_x$ compounds are compared, one finds in both cases a first positive peak at the absorption threshold, while the remaining signal is a splitted peak exhibiting two lobules of different sign. The sign of these lobules is opposite for light and heavy rare earths (see Fig. 1). The systematic study of the Fe K -edge XMCD through the

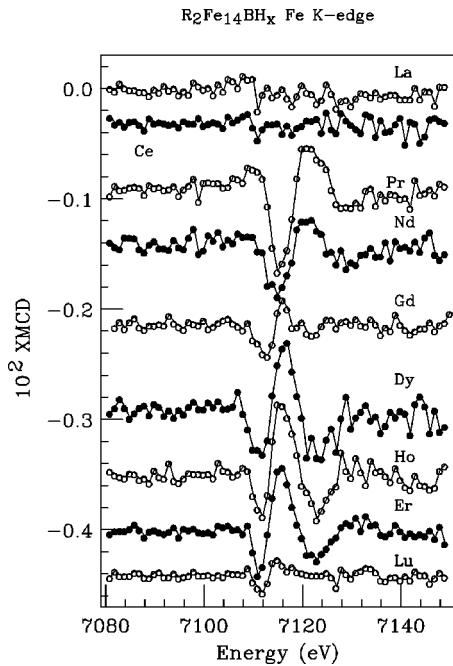


FIG. 2. Normalized x-ray magnetic circular dichroism spectra at the Fe K edge for the $R_2\text{Fe}_{14}\text{BH}_x$ compounds after the subtraction of the $\text{Y}_2\text{Fe}_{14}\text{BH}_x$ XMCD signal. The scale ($\times 10^2$) is referred to the $R = \text{La}$ case.

$R_2\text{Fe}_{14}\text{BH}_x$ series, illustrated in Fig. 1 shows that the shape of the dichroic spectra is markedly different as a function of the rare-earth nature, i.e., nonmagnetic, light, and heavy rare-earth cases, being in agreement with that previously observed in the case of the pure $R_2\text{Fe}_{14}\text{B}$ compounds.¹⁷

According to the results obtained in Ref. 17 we have performed a two-magnetic sublattice analysis of the XMCD signals. In this framework, the total magnetization of the $R_2\text{Fe}_{14}\text{BH}_x$ systems is assumed to be the addition of both iron and R sublattice magnetizations, i.e., $M_T = M_R + M_{\text{Fe}}$. An estimate for the average magnetization of the Fe sublattice in the series is given by the magnetizations of the $R = \text{La}, \text{Ce}, \text{Lu},$ and Y compounds, because those materials can be regarded as magnetically blank with respect to the rare-earth component. For the compounds in which the rare-earth supports a moment the R -sublattice magnetization can be estimated by subtracting the saturation magnetization of Y from the other $R_2\text{Fe}_{14}\text{BH}_x$ magnetizations.⁴ In this way, we have considered that the Fe K -edge XMCD spectrum in these $R_2\text{Fe}_{14}\text{BH}_x$ compounds corresponds to the addition of the magnetic contribution of both Fe and R sublattices. Thus, we have subtracted the Fe K -edge XMCD signal of $\text{Y}_2\text{Fe}_{14}\text{BH}_x$ from those of the other $R_2\text{Fe}_{14}\text{BH}_x$ materials. The result of this procedure is reported in Fig. 2. Within the current framework, the remaining XMCD signal after subtraction would correspond to the rare-earth sublattice magnetic contribution. In the case of the nonmagnetic R -based compounds, La and Ce , the signals obtained in this way are zero within the signal-to-noise ratio. This result supports the validity of our assumption to extract the Fe sublattice magnetization from the Y -based compound. For the light- R hydrides Pr and Nd the residual signal shows a negative peak at about 7 eV above the edge, and a positive peak at ~ 13 eV above the edge. On the contrary, in the heavy rare-earth compounds, the negative peak is strongly depressed while a posi-

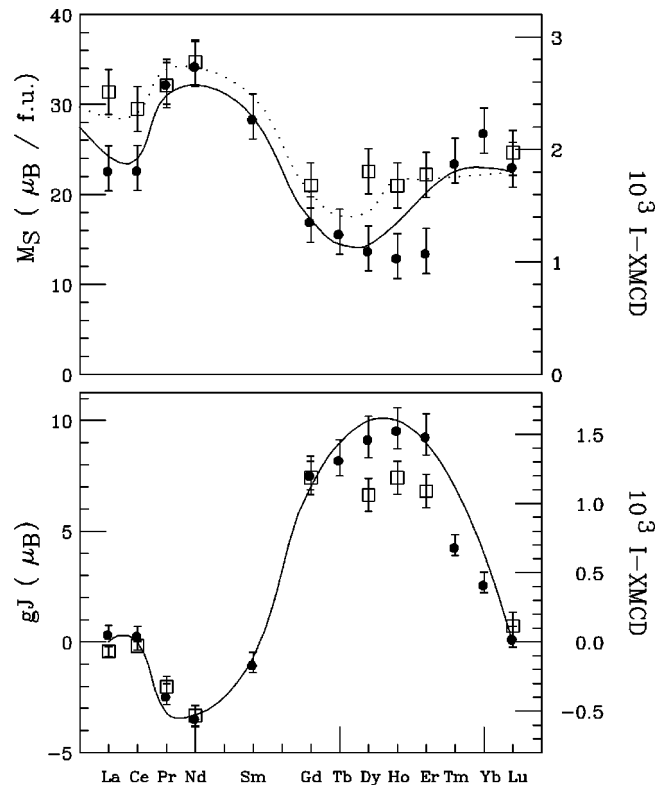


FIG. 3. Top panel. Comparison of the saturation magnetization of the $R_2\text{Fe}_{14}\text{B}$ compounds (solid) and their hydride derivatives (dotted line) and the integrated XMCD signals for the pure (circles) and hydrided (open squares) compounds. Bottom panel: Comparison between the rare-earth magnetic moments gJ according with Russel-Saunders coupling (solid line) and those derived from the Fe K edge integrated XMCD signal for the $R_2\text{Fe}_{14}\text{B}$ (circle) and their hydride derivatives (open squares), after the subtraction the XMCD signal of the corresponding Y -based compound (see text for details).

tive peak arises at about 7 eV above the edge. These results are consistent with both the different shape of the dichroic spectra as a function of the rare-earth nature (nonmagnetic, light, and heavy), and the different coupling of the rare-earth and iron sublattices in light and heavy rare-earth $R_2\text{Fe}_{14}\text{BH}_x$ compounds.

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. It has been recently proposed that the Fe K -edge XMCD signals are directly related to the Fe $(4p,3d) - R(5d)$ hybridized band, so 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.¹⁷ If so, the extracted signals should be related to the magnitude of the R magnetic moments and furthermore, it would be possible to monitor the modification of the rare-earth magnetic moment upon hydrogen absorption in these $R_2\text{Fe}_{14}\text{BH}_x$ intermetallic compounds. In order to obtain a deeper insight on this behavior, we have compared the integrated Fe K -edge signals to the saturation magnetization data previously reported for the $R_2\text{Fe}_{14}\text{BH}_x$ hydrides.¹⁴ For the sake of completeness we also show both XMCD and magnetization data of the pure, nonhydrided, $R_2\text{Fe}_{14}\text{B}$ compounds.^{14,17} The evolution of the integrated XMCD across the 2:14 series, shown in Fig. 3, is in agree-

ment with that of the magnetization, showing a depletion of both magnetic signals for the heavy rare-earth compounds, as expected due to the antiferromagnetic coupling of Fe and R magnetic moments. Moreover, the magnetization increase observed upon hydriding is exhibited by the integrated XMCD signals as well. Moreover, we have performed the integration of the remaining XMCD signals after the subtraction of the Fe K -edge XMCD signal of $Y_2Fe_{14}BH_x$ (Fig. 2), to be compared to the rare-earth magnetic moments corresponding to the Russel-Saunders coupling scheme. This procedure has been performed for both the parent $R_2Fe_{14}B$ compounds and their hydrides derivatives $R_2Fe_{14}BH_x$. The comparison between the theoretical μ_R and those derived from the XMCD data is shown in Fig. 3. As shown in this figure, there is a good agreement between the theoretical $\mu_R = g_J J$ and those values derived from the magnetization and XMCD data for the parent $R_2Fe_{14}B$ compounds. It is important to note also, how the integrated XMCD signal associated to the rare-earth changes sign from the light- R compounds (negative) to the heavy- R compounds (positive), in agreement with the ferromagnetic (antiferromagnetic) coupling of the R and Fe magnetic moments for light (heavy) rare-earth compounds.

One of the most striking consequences of our study, identifying the influence of the rare-earth magnetic state into the Fe K -edge XMCD signals, resides in the possibility to derive some information regarding the change of the rare-earth magnetic moment upon hydrogen absorption. As shown in Fig. 3, both magnetization and XMCD data are consistent with the depletion of the rare-earth magnetic moment upon hydriding. This result is in agreement with ^{161}Dy and ^{166}Er Mössbauer experiments showing that the hyperfine field, providing direct information about the local magnetic moment, at the rare-earth sites are significantly reduced.^{10,11} Moreover, the observed reduction of the rare-earth magnetic

moment is seen to be different for light and heavy rare earths. Indeed, while the reduction of μ_R for Nd and Pr is less than 10% as derived from both XMCD and magnetization analyses, whereas for the heavy rare earths it is of the order of 25%. This behavior, showing a stronger influence of the interstitial hydrogen on the heavy rare earths, can be explained in terms of the different hydrogen filling sequence. When R is a light rare earth, hydrogen fills preferentially the $16k$ sites having two R and two Fe nearest neighbors,¹⁸ while in the case of a heavy rare earth the $8j$ sites, with three R and one Fe nearest neighbors, are preferentially filled.¹⁹

Summarizing, in this work we have presented a detailed x-ray magnetic circular dichroism (XMCD) study at the iron K edge in the hydride derivatives of the $R_2Fe_{14}B$ series. This study identifies the influence of the rare-earth magnetic state into the Fe K -edge XMCD signals in hydrides derivatives of R -Fe intermetallic compounds. In agreement with a previous report,¹⁷ the XMCD signal has been identified as being due to the addition of the magnetic contribution of both the Fe and R sublattices. The contribution of the R sublattice to the XMCD signal has then been extracted yielding a direct correlation to the R magnetic moment, which is determined to decrease upon hydrogen absorption in these materials. Our analysis, showing a depressed rare-earth moment in the hydrides, is in agreement with the results inferred from both saturation magnetization and rare-earth Mössbauer hyperfine field data. Moreover, the observed trend across the hydride series show how the influence of hydrogen on the rare-earth magnetic moment is different for light and heavy rare earths, in agreement with magnetization data and the different filling sequence.

We are indebted to T. Iwazumi for the experimental support at KEK. This work was partially supported by the INFN-CICYT Agreement and Spanish DGICYT Grant No. MAT96-0448.

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