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Enhancement of anisotropy in $Nd_2Fe_{14}B$ driven by Eu substitution

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The Eu substitution for Nd in $Nd_2Fe_{14}B$ leads to the decrease of the magnetization of the system. This reduction is in agreement with the dilution of the Nd sublattice magnetization by a nonmagnetic ion. However, contrary to the behavior found for the substitution of Nd by nonmagnetic species, no decrease of the magnetocrystalline anisotropy is found upon Eu substitution. Indeed, the strength of the anisotropy field at room temperature is enhanced in the Eu substituted compounds. We determined by x-ray-absorption spectroscopy at the Eu L_3-edge that the electronic state of the Eu ion in the metallic $Nd_2Fe_{14}B$ host is trivalent. Our results suggest the role of a non-negligible orbital contribution of Eu ions that can be explained by taking into account the mixing of the lowest spin-orbit multiplets of Eu^{3+}.

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$Nd_2Fe_{14}B$ compound has been the center of recent research of magnetic materials with permanent magnet properties. Special interest has been focused on the modification of its magnetic properties under the substitution of both Nd and Fe by other rare earths and transition metals, respectively. Most of the substitutions have been tailored with the aim of understanding the physics of the magnetic anisotropy and the origin of the spin reorientation transition (SRT). The SRT takes place below $T_{SRT} \sim 135$ K and, as the magnetization deviates from the crystallographic *c* axis, the uniaxiality is lost and the magnet performance worsens.[1]

As a result of substitution of Nd by other nonmagnetic rare earth or Y, both the whole magnetization and the magnetocrystalline anisotropy of the system are strongly reduced.[2,3] In addition, such a substitution weakens the SRT transition which takes place at lower temperatures. In this paper, we report on the influence of europium substitution for neodymium in $Nd_2Fe_{14}B$, which gives rise to a peculiar magnetic behavior. In particular, while the substitution depresses magnetization, the magnetocrystalline anisotropy is preserved. The combined study of macroscopic magnetic properties and x-ray-absorption spectroscopy (XAS) determines that these peculiarities can be attributed to the presence of trivalent Eu. In addition, our results point out to the role of the orbital momentum of Eu even when $J=0$ in the ground state throughout the $Nd_{2-x}Eu_xFe_{14}B$ series.

The $Nd_{2-x}Eu_xFe_{14}B$ alloys ($x=0$, 0.2, 0.8) and $Y_2Fe_{14}B$ were prepared by melting the pure elements in a high-frequency induction furnace, under Ar protective atmosphere. In the case of the Eu-containing compounds, prealloys of (Nd,Eu) were prepared using Eu excess amounts in order to compensate for the losses (mainly in Eu) by evaporation during melting and annealing, due to its high vapor pressure. The Eu excess amounts were tailored by trial for each stoichiometry, so that the estimated shifts in the rare-earth content from the nominal stoichiometry to be less than 5% in the annealed samples. The as-cast alloys were wrapped in Ta foil and enclosed in silica tubes, under Ar gas. Pure $Y_2Fe_{14}B$ and $Nd_2Fe_{14}B$ compounds were annealed at 950 °C, while $Nd_{2-x}Eu_xFe_{14}B$ compounds were annealed at 800 °C for two weeks and then quenched to room temperature.

Structural characterization was performed at room temperature by means of powder x-ray diffraction, using a rotating-anode Rigaku diffractometer in the Bragg-Brentano geometry, with Cu-$K\alpha$ radiation. The diffraction patterns were Rietveld refined using the FULLPROF code.[4] We found that the majority phase with a $Nd_2Fe_{14}B$ structure was formed in all the $Nd_{2-x}Eu_xFe_{14}B$ samples, the presence of secondary phases being (α-Fe and 2:17) less than $<8\%$ overall.

The magnetic measurements were performed by using a commercial superconducting quantum interference device magnetometer (Quantum Design MPMS-S5). Magnetic isotherms were measured on loose powders in applied magnetic fields $H \leqslant 5$ T. The saturation magnetization M_S was derived from Honda (M vs $1/H$) plots and subsequent correction for the free iron content as given by the refinement of the x-ray-diffraction (XRD) data.[5] The same powders were used for magnetization measurements performed on magnetically aligned samples. For these measurements cylindrical-shaped samples consisted of powders with a grain size of less than 20 μm embedded in epoxy resin and aligned in a magnetic field on about 0.5 T with the axis of the cylinder parallel and perpendicular, respectively, to the field direction at the room temperature were used. The Curie temperature was determined from thermomagnetic curves measured with a Faraday-type balance between room temperature and 1073 K, and by using Ni standard as reference.

X-ray-absorption spectroscopy (XAS) experiments were carried out at the ESRF BM29 XAFS beamline. The storage ring was operated in 16 bunch mode with typical current of ~ 90 mA at an electron beam energy of 6 GeV. XAS experiments were performed in the fluorescence detection mode on powder samples at the Eu L_3-edge. The fixed-exit double-

TABLE I. Lattice constants, c/a ratio, unit-cell volume, magnetic ordering (T_c), and spin reorientation temperatures (T_{SRT}) of the $Nd_{2-x}Eu_xFe_{14}B$ and $Y_2Fe_{14}B$ compounds.

Compound	a (Å)	c (Å)	c/a	V(Å^3)	T_c (K)	T_{SRT} (K)
$Y_2Fe_{14}B$	8.7455(4)	12.015(1)	1.374	918.9(1)	574±2	
$Nd_2Fe_{14}B$	8.7986(3)	12.189(1)	1.385	943.6(1)	593±2	137±2
$Nd_{1.8}Eu_{0.2}Fe_{14}B$	8.8033(4)	12.198(1)	1.386	945.3 (1)	594±2	139±2
$Nd_{1.2}Eu_{0.8}Fe_{14}B$	8.8039(8)	12.203(2)	1.386	945.9(2)	591±2	136±2
Ni					627±2	

crystal monochromator was equipped with a pair of Si (311) crystals with the energy resolution $\Delta E/E \sim 7\times 10^{-5}$ at the Eu L_3-edge (6977 eV). The harmonics rejection was achieved by detuning the second crystal from the parallel alignment to 50% intensity. Fluorescence spectra were recorded with the sample aligned at 45° with respect to the incident beam, using a 13-element Ge solid state detector (Canberra) with an energy resolution ~300 eV. At least 12 fluorescence scans were recorded and averaged for the Eu-subtituted sample. Fluorescence spectra were also recorded on EuF_2 and EuF_3 pellets, as reference for the determination of the Eu oxidation state.

Lattice parameters and magnetic transition temperatures of the $Nd_{2-x}Eu_xFe_{14}B$ series and $Y_2Fe_{14}B$ compound are summarized in Table I. The Curie temperature T_C was determined at the inflection point of the magnetization vs temperature drop. The spin reorientation temperature was determined from the inflection point in magnetization vs temperature curves measured in an applied field of 0.1 T. In the case of the Eu-doped samples, both T_C and T_{SRT} remain unaltered, within the experimental error, with respect to those of the pure $Nd_2Fe_{14}B$ compounds. This behavior is rather surprising. Indeed, both T_C and T_{SRT} are linearly reduced through the $Nd_{2-x}Y_xFe_{14}B$ series when increasing the Y content.[2,3,6] In particular, for Y concentrations between $x = 0.5$ and 1, the decrease of T_{SRT} is reported to be ~15 K (Refs. 2, 3, and 6) ($\Delta T_{SRT} \sim 10\%$).

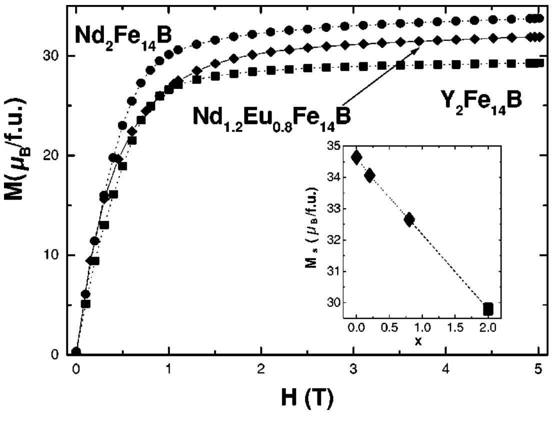

FIG. 1. Room-temperature magnetization curves of $Nd_2Fe_{14}B$ (●), $Nd_{1.2}Eu_{0.8}Fe_{14}B$ (♦), and $Y_2Fe_{14}B$ (■). In the inset the dependence of the saturation magnetization M_S of the $Nd_{2-x}Eu_xFe_{14}B$ series (♦) with Eu content is shown. For the sake of clarity the data for $Y_2Fe_{14}B$ is also displayed (■).

The behavior of the magnetization vs applied magnetic field for the $Nd_{2-x}Eu_xFe_{14}B$ compounds is shown in Fig. 1. The magnetization decreases progressively as Eu content increases. In order to sort out the magnetic contribution of the rare-earth sublattice, we have applied the standard two sublattice model to the analysis of the saturation magnetization (M_S), obtained from Honda (M vs $1/H$) plots. Hence we assume that the total magnetization of the $Nd_{2-x}Eu_xFe_{14}B$ compounds is the sum of the rare-earth and iron sublattice magnetizations, the latter one assumed to be identical to that of $Y_2Fe_{14}B$ at each temperature. As shown in Table II, according to the above approximations, the values derived for μ_{Nd} are consistent with Eu in nonmagnetic state throughout the $Nd_{2-x}Eu_xFe_{14}B$ series. Surprisingly, while the behavior of M_S as a function of the Eu content reveals a real magnetic dilution of the Nd ion (see inset of Fig. 1), as in the case of Nd dilution by nonmagnetic elements like Y, the fact that both T_C and T_{SRT} remain constant through the $Nd_{2-x}Eu_xFe_{14}B$ series suggests the contrary.

In addition, Fig. 2 shows the magnetization curves measured on magnetically aligned samples, with the field applied parallel, $M\|$ and perpendicular, $M\perp$, to the crystallographic c axis for $Y_2Fe_{14}B$ and $Nd_{2-x}Eu_xFe_{14}B$ compounds at RT. Following Franse and Radwanski[7] the anisotropy field H_A is obtained, by definition, as the crossing point of the extrapolated low-field hard-axis magnetization curve with the easy-direction magnetization curve. The values derived for H_A are summarized in Table II. While Eu substitution leads to the decrease of magnetization, the anisotropy field is found to increase through the $Nd_{2-x}Eu_xFe_{14}B$ series.

This result is again surprising as compared to previous studies on the effect of diluting Nd by a nonmagnetic ion in $Nd_2Fe_{14}B$; see Fig. 3. Most of this research deals with the

TABLE II. Magnetic properties of $Nd_{2-x}Eu_xFe_{14}B$ compounds.

Compound	T (K)	$M_s(\mu_B/\text{f.u.})$	$\mu_{Nd}(\mu_B)$	H_a (kOe)
$Y_2Fe_{14}B$	300	29.79		18.5
	4.2	33.38		11.5
$Nd_2Fe_{14}B$	300	34.64	2.4	69.5
	4.2	39.62	3.1	
$Nd_{1.8}Eu_{0.2}Fe_{14}B$	300	34.06	2.4±0.10	70
	4.2	38.68	3.0±0.15	
$Nd_{1.2}Eu_{0.8}Fe_{14}B$	300	32.65	2.4±0.10	73
	4.2	37.40	3.3±0.15	

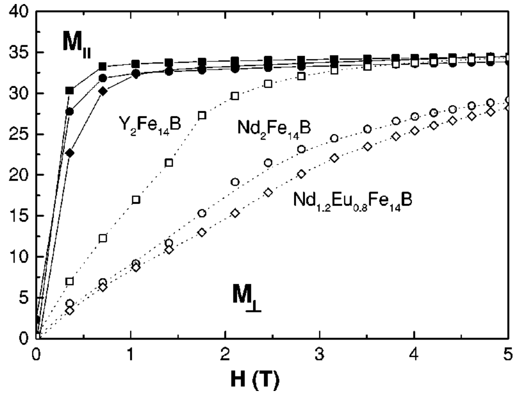

FIG. 2. Room-temperature magnetization curves of magnetically aligned powders with the field applied parallel, M∥ (solid symbols), and perpendicular, $M\perp$ (open symbols), to the c axis: $Nd_2Fe_{14}B$ (●), $Nd_{1.2}Eu_{0.8}Fe_{14}B$ (◆), and $Y_2Fe_{14}B$ (■).

$Nd_{2-x}Y_xFe_{14}B$ series in which Nd is subtituted by yttrium.[2,6,8] The main results of this substitution can be summarized as follows: T_C of the Nd-Y series decreases almost linearly with the increase of the yttrium content; the saturation magnetization decreases with decreasing Nd content; the magnetic moments per iron or Nd are not much altered by the substitution of the nonmagnetic yttrium; and, finally, a very sharp linear decrease in H_A is observed with the increase of the Y content (Fig. 3). Moreover, the reduction of H_A in $Nd_{2-x}R_xFe_{14}B$ has been also reported even for magnetic ions ($R=$Gd, Ho, Er) together with the relative decrease of T_{SRT}.[3] On the contrary, Nd substitution by Dy in $(Nd_{1-x}Dy_x)_2Fe_{14}B$ leads to the decrease of magnetization but to the increase of the anisotropy field.[9]

The variation of T_C induced in $Nd_2Fe_{14}B$ for substitution of Nd with a nonmagnetic rare-earth element shows that the scale of T_C for the series is mainly set by the exchange interaction between the iron spins,[1] while the magnetocrystalline anisotropy and the SRT transitions, instead, must be dominated by the rare-earth contribution. However, the fact that Eu substitution exerts smaller influence on the SRT transition than Y substitution in $Nd_2Fe_{14}B$ and the observed enhancement of H_A when increasing the Eu content indicate that Eu behaves not as a simple nonmagnetic ion. Contrary to the behavior observed in the case of the $(Nd,Y)_2Fe_{14}B$ series, the Eu substitution does not determine the decrease of both the Curie and SRT transition temperatures. In addition, the observed enhancement of H_A at RT when increasing the Eu content indicates that Eu has a behavior different from that of a simple nonmagnetic ion. Indeed, substituting Nd by a nonmagnetic element such as Y or La reduces the anisotropy field, as expected if the main part of the anisotropy was due to the Nd single-ion anisotropy. Moreover, a similar behavior has been found when the Nd sublattice anisotropy is diluted by Gd, which is a spin-only ion.[2]

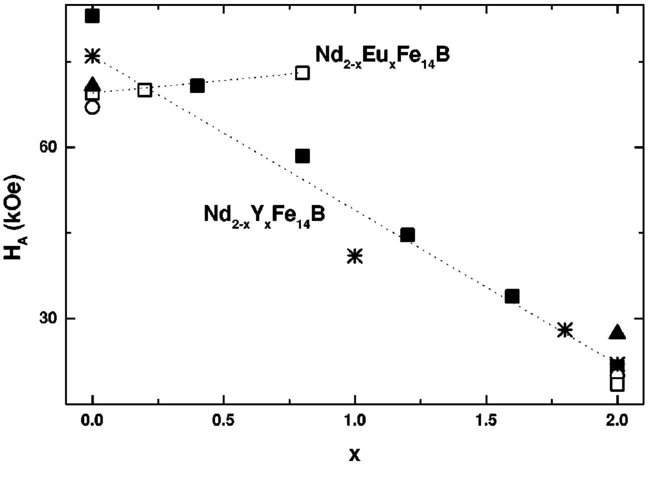

FIG. 3. Comparison of the anisotropy field of $Nd_{2-x}Eu_xFe_{14}B$ (□) and $Nd_{2-x}Y_xFe_{14}B$. The data for the Nd-Y substitution has been taken from Ref. 6 (■) and Ref. 3 (★). In addition, data for the pure $Nd_2Fe_{14}B$ and $Y_2Fe_{14}B$ taken from Ref. 13 (●) and Ref. 14 (▲) are also shown.

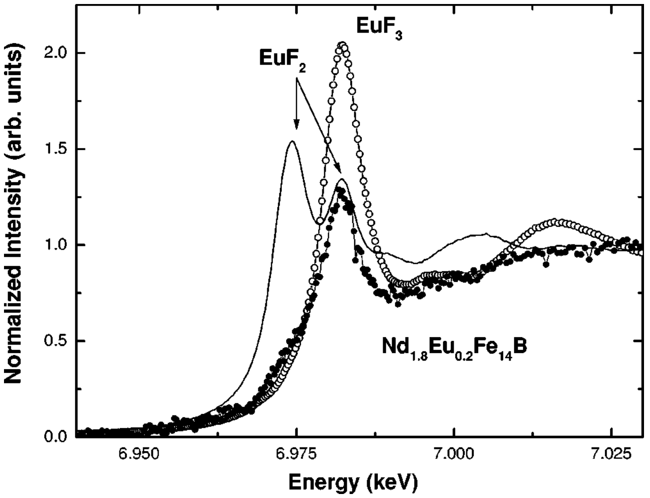

FIG. 4. Eu L_3-edge x-ray appearance near-edge structure spectra of EuF_2 (solid line), EuF_3 (○), and $Nd_{1.8}Eu_{0.2}Fe_{14}B$ (●) at room temperature.

In order to get a deeper insight on the origin of this peculiar behavior it is needed to establish the electronic state of Eu in these materials since europium can be present as divalent magnetic Eu^{2+} ($L=0$, $S=7/2$, $J=7/2$) or as trivalent nonmagnetic Eu^{3+} ($L=3$, $S=3$, $J=0$). To this aim we have recorded the Eu L_3-edge absorption spectra in the $Nd_{2-x}Eu_xFe_{14}B$ samples as well as in the references EuF_2 and EuF_3. The Eu L_3 absorption line in the EuF_3 compound, shown in Fig. 4, exhibits at the absorption threshold the characteristic single and pronounced peak of trivalent rare-earth ions.[10] By contrast, the L_3 absorption spectrum of Eu in EuF_2 exhibits the typical double peak at the edge characteristic of mixed-valent Eu.[10] From this figure it is clear that Eu in the $Nd_{2-x}Eu_xFe_{14}B$ series behaves as Eu^{3+} in EuF_3. This spectrum can be also directly compared to that of Eu_2O_3,[10] thus suggesting a trivalent valence state for Eu through the $Nd_{2-x}Eu_xFe_{14}B$ series. It is likely that the presence of trivalent Eu in the $Nd_{2-x}Eu_xFe_{14}B$ series could explain why Y and Eu substitutions influence differently on the spin reorientation transition and the anisotropy field in both Y and Eu series. To this respect it should be noted that despite being trivalent the magnetic properties of Eu do not simply correspond to the nonmagnetic $(J=0)$ $^7F_0$ Hund-rule $^4f_6$ ground state. Eu^{3+} differs from the other trivalent rare-earth ions in having the multiplet intervals comparable to kT in such a way that due to the multiplets mixing not only the ground state is populated at room temperature[11] but excited states may be populated as well. Therefore the enhancement of the magnetocrystalline anisotropy in the $(Nd_{2-x}R_x)Fe_{14}B$ series when increasing the Eu content may be possibly accounted for in terms of an orbital contribution of the Eu ions. In addition, detailed heat-capacity studies of the $R_2Fe_{14}B$ series near the magnetic ordering temperature reveal an anomalous entropy contribution that is explained in terms of the contribution of the rare-earth spin.[12] The fact that T_C is not affected by Eu substitution through the $(Nd_{2-x}R_x)Fe_{14}B$ series should be in agreement with a magnetic contribution coming from Eu ions.

In summary, we have studied the influence of europium substitution for Nd on the magnetic properties of $Nd_2Fe_{14}B$. Eu substitution in $Nd_2Fe_{14}B$ carries the main hallmarks of diluting Nd by a nonmagnetic ion as magnetization decreases upon increasing the Eu content. This result is in agreement with x-ray-absorption spectroscopy studies showing that the electronic state of Eu within $Nd_{2-x}Eu_xFe_{14}B$ series is trivalent, thus ruling out the presence of divalent magnetic Eu^{2+}. Both the magnetic ordering and spin reorientation transitions are not affected by Eu substitution, while the anisotropy field of the system is found to increase as Eu content does. The peculiar magnetic behavior of the $Nd_{2-x}Eu_xFe_{14}B$ series suggests the existence of spin and orbital Eu contributions to the system that can be explained by taking into account the mixing of the lowest spin-orbit multiplets of Eu^{3+}.

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