Effect of pressure on the magnetocrystalline anisotropy of (Er$_x$R$_{1-x}$)$_2$Fe$_{14}$B intermetallics

Effect of pressure on the magnetocrystalline anisotropy of $(Er_xR_{1-x})_2Fe_{14}B$ intermetallics

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Abstract. A systematic study of the effect of pressure up to 1 GPa on the spin reorientation transition (SRT) phenomena has been performed on several series of pseudo-ternary compounds $(Er_xR_{1-x})_2Fe_{14}B$ for R ≡ Nd, Gd, Dy and Y using a low-field AC susceptibility technique. The variation in the SRT temperature T_{SR} under pressure has been used as an indication of the effect of the pressure on the crystal electric field (CEF) at the rare-earth ion site. We have observed that the pressure effect on the $Er_2Fe_{14}B$ compound $(\Delta T_{SR}/\Delta p = -20$ K GPa$^{-1})$ was not affected by the substitution of Er by Gd and Y ions. A completely different high-pressure behaviour has been observed for the $(Er_xDy_{1-x})_2Fe_{14}B$ and $(Er_xNd_{1-x})_2Fe_{14}B$ compounds, in which the variation in T_{SR} under pressure decreases for increasing content of Dy and Nd. This different behaviour has been attributed to the strong influence of pressure on the CEF interactions. Using these results we have determined the variation in the CEF parameters under applied pressure.

1. Introduction

The intermetallic compounds $R_2Fe_{14}B$ (where R is a rare earth or yttrium) with a characteristic tetragonal crystal structure (space group, $P4_2/mnm$) exhibit not only outstanding magnetic properties for permanent magnet applications such as high magnetocrystalline anisotropy and a large magnetic moment per formula unit (Mitchell *et al* 1989, Herbst 1991), but also complex magnetic phenomena such as the spin reorientation transitions (SRT) (Hirosawa and Sagawa 1985, Hirosawa *et al* 1986), first-order field-induced magnetization processes (Pareti *et al* 1985, Radwanski and Franse 1988) and large magnetovolume effects (Givord *et al* 1984, Buschow 1986, Algarabel *et al* 1992).

The origin of the anisotropy energy in $R_2Fe_{14}B$ compounds is not completely clear yet. The observed anisotropic behaviour is usually described in terms of two main contributions. One of them arises from the anisotropic 4f charge cloud of the rare-earth ions and the other has its origin in the 3d electron bands. The rare-earth magnetic sublattice exhibits planar (Sm, Tm and Er), axial (Dy and Pr), cone (Nd and Ho) or negligible (Gd and Y) anisotropies. This contribution is, in general, dominant at low temperatures and the easy magnetization direction (EMD) for the rare-earth magnetic moment μ_R depends on the sign of the second-order Stevens

factor α_J of the trivalent rare-earth ion. The other important contribution to the overall magnetocrystalline anisotropy has its origin in the 3d sublattice and tends to align the Fe magnetic moments μ_{Fe} along the c axis. The interplay between the magnetocrystalline anisotropies of the different magnetically ordered sublattices leads to SRT phenomena of different nature, in which the EMD for the total magnetic moment $\mu = \mu_R + \mu_{Fe}$ spontaneously changes at T_{SR}.

In order to study the nature of the anisotropic behaviour of the $R_2Fe_{14}B$ compounds, extensive studies of the SRT were carried out, not only for $R_2Fe_{14}B$ but also for the pseudo-ternary $(R_xR'_{1-x})_2Fe_{14}B$ compounds. R and R' represent rare-earth ions with α_J of opposite signs, such as $(Er_xDy_{1-x})_2Fe_{14}B$ or $(Er_xNd_{1-x})_2Fe_{14}B$ (Niarchos and Simopoulos 1986, Boltich *et al* 1987, Rechenberg *et al* 1987, Ibarra *et al* 1988, 1989, del Moral *et al* 1989, Marusi *et al* 1990). These studies revealed complicated magnetic phase diagrams as a function of temperature and concentration, in which axial, plane and cone regions were observed. Axial and plane regions correspond to intervals of temperature and concentration in which μ is along either the c axis or a direction in the basal plane, respectively. The cone region is characterized by an alignment of μ along a non-major symmetry direction. As a consequence, a non-collinear arrangement of μ_R and μ_{Fe} is established.

The distance dependence of the Fe–Fe exchange interaction has been studied by various kinds of experiment: thermal expansion in the ordered regime (Buschow 1986, Algarabel *et al* 1992), magnetization measurements (Gavigan *et al* 1988) and pressure dependence of the Curie temperature T_C (Kamarad *et al* 1987). In the case of the $Nd_2Fe_{14}B$ compound a large decrease under pressure in T_C ($\Delta T_C/\Delta p = -26.5$ K GPa^{-1} (Kamarad *et al* 1987)) was observed. Nevertheless, no variation in T_{SR} was found. We have recently observed a significant decrease in T_{SR} with increasing pressure ($\Delta T_{SR}/\Delta p = -20$ K GPa^{-1}) for $Er_2Fe_{14}B$ (Arnold *et al* 1991, Ibarra *et al* 1992a). These different high-pressure behaviours concerning the change in T_{SR} seem to be related to the different characters of the SRT in the two compounds.

Since the SRT takes place in the ordered regime, both CEF and exchange interactions, in principle, will be modified by the pressure. One purpose of this work is to elucidate which of these interactions is more relevant in the framework of the observed phenomena. To obtain a better insight into these problems, we have performed a systematic high-pressure study of pseudo-ternary $(Er_xR_{1-x})_2Fe_{14}B$ compounds with different R substitutions. We have studied two types of compound in which the Er sublattice is diluted either by isotropic R ions (R $\equiv$ Y, Gd) or by anisotropic ions with α_J of opposite signs (R $\equiv$ Nd, Dy).

The analysis of the experimental results has been undertaken using a single-ion CEF mean-field model in order to explain the spontaneous variation in T_{SR} in the $(Er_xY_{1-x})_2Fe_{14}B$ and $(Er_xGd_{1-x})_2Fe_{14}B$ series of compounds. Using this model we also accounted for the variation in T_{SR} with pressure, which allowed us to determine the pressure dependence of the CEF parameters.

2. Experimental details and results

The polycrystalline samples of $(Er_xY_{1-x})_2Fe_{14}B$ with $x = 1$, 0.8, 0.6, 0.4, 0.2, of $(Er_xGd_{1-x})_2Fe_{14}B$ with $x = 0.8$, 0.6, 0.4, 0.2, of $(Er_xDy_{1-x})_2Fe_{14}B$ with $x = 0.9$, 0.8, 0.7 and of $(Er_xNd_{1-x})_2Fe_{14}B$ with $x = 0.8$, 0.7, 0.6, 0.5, 0.3, 0.2, 0 were prepared by the standard arc melting technique and annealed at 850 °C. The quality of the samples obtained was tested by x-ray and microprobe analysis.

The permeability method was used for the determination of T_{SR}. The sample formed the core of a microtransformer with seven turns in both primary and secondary coils. An AC current of 10 mA with frequency 1 kHz was kept constant in the primary coil. The T_{SR} was defined as the maximum in the susceptibility versus temperature plot. The high-pressure measurements were made in a CuBe cell with fixed hydrostatic pressure up to 1 GPa. The pressure and temperature were measured *in situ* using a manganin pressure sensor and a Ni–(Ni–Cr) thermocouple, respectively.

To determine in more detail the character of the SRT in the compounds studied, magnetically aligned samples of $(Er_{0.2}Y_{0.8})_2Fe_{14}B$ and $(Er_{0.2}Gd_{0.8})_2Fe_{14}B$ were prepared by orienting fine powders of the samples using epoxy resin in a constant magnetic field of 5 kOe at room temperature. In addition, for these samples, polar plots of the magnetization parallel $(M_\parallel)$ and perpendicular $(M_\perp)$ to the applied magnetic field (1 kOe) direction were obtained at different temperatures using an extraction magnetometer (del Moral *et al* 1988, Joven *et al* 1990). The results obtained are summarized in figure 1 where the variation in the SRT is shown for different concentrations of R ions. The nature of the magnetic phase below T_{SR} is different depending on the character of the anisotropy of the R ion involved and will be discussed below.
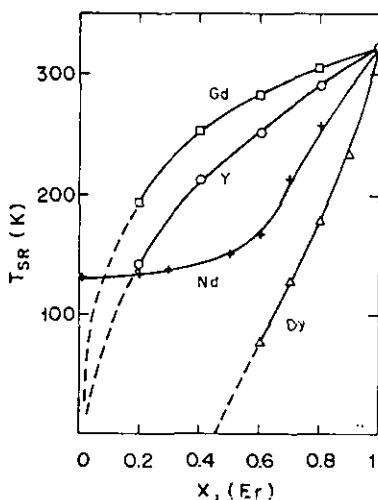

Figure 1. Dependence of the T_{SR} on the R content for different $(Er_xR_{1-x})_2Fe_{14}B$ compounds: O, Y; □, Gd; △, Dy; +, Nd; ——, guides for the eye.

As one can expect from the dilution of the Er^{3+} ions using either an anisotropic or an isotropic ion, the overall anisotropic behaviour will be drastically modified. In the case of the dilution using either Dy or Nd, we reinforce the axial anisotropy as we increase the concentration of such ions. As a consequence a new balance between the Er–R–Fe magnetic free-energy contributions will be established and will cause a decrease in T_{SR}. This simple picture has its origin in the hypothesis of a single-ion origin for the anisotropy of the 4f ions in the intermetallic compounds and it has been extensively tested in mixed $(R–R')_2Fe_{14}B$ compounds (Rechenberg *et al* 1987, Ibarra *et al* 1988, 1989, Boltich *et al* 1987). A similar behaviour can be expected when
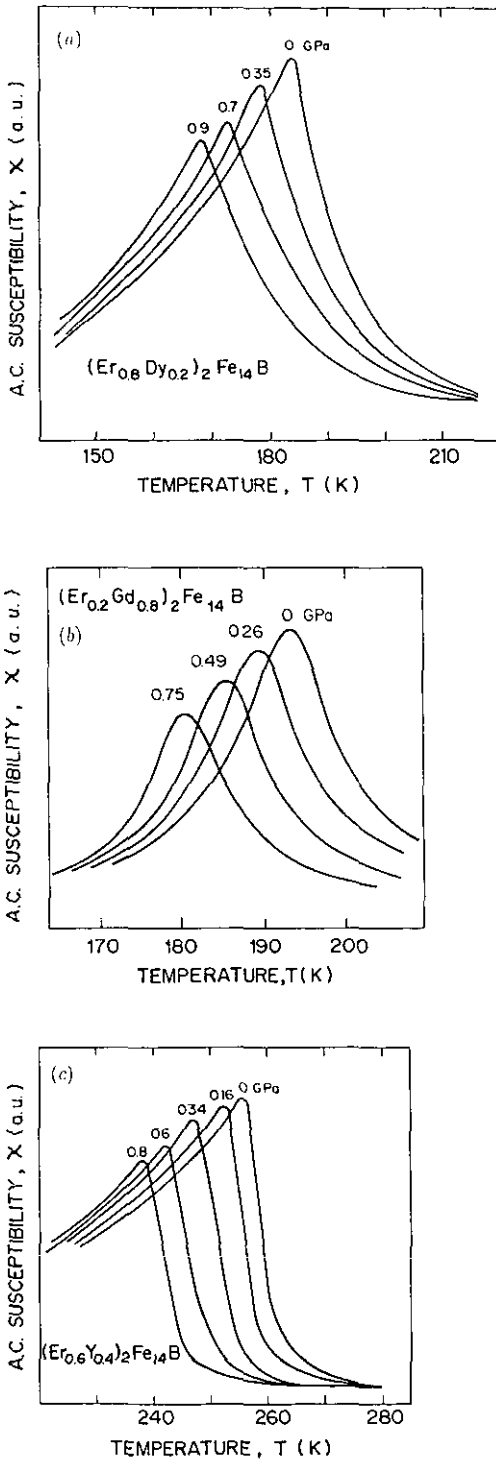
Figure 2. Temperature dependence of the AC susceptibility for some selected compounds under several hydrostatic pressures (a.u., arbitrary units): (*a*) $(Er_{0.8}Dy_{0.2})_2Fe_{14}B$; (*b*) $(Er_{0.2}Gd_{0.8})_2Fe_{14}B$; (*c*) $(Er_{0.6}Y_{0.4})_2Fe_{14}B$.

substituting with isotropic ions such as Gd and Y. In this case we found a weakening of the planar anisotropy of the Er sublattice.

In general, the investigated compounds $(Er_xR_{1-x})_2Fe_{14}B$ with R $\equiv$ Nd, Gd, Dy and Y present a decrease in T_{SR} with increasing pressure. $Nd_2Fe_{14}B$ is the only exception where no variation was observed. In figure 2 we display the thermal dependence of the AC magnetic susceptibility for different values of the hydrostatic pressure for some selected compounds $(Er_{0.8}Dy_{0.2})_2Fe_{14}B$ (figure 2(*a*)), $(Er_{0.2}Gd_{0.8})_2Fe_{14}B$ (figure 2(*b*)) and $(Er_{0.6}Y_{0.4})_2Fe_{14}B$ (figure 2(*c*)). The dependence of T_{SR} on pressure for all the compounds studied is linear. In figure 3 the pressure dependence of T_{SR} for compounds in the series $(Er_xDy_{1-x})_2Fe_{14}B$ is shown. The slopes $\Delta T_{SR}/\Delta p$ of the straight lines are represented in figure 4 for the series of compounds studied. The values obtained for T_{SR} and $\Delta T_{SR}/\Delta p$ are also summarized in table 1.

Table 1. Experimental values (T_{SR}^{exp}) and calculated values (T_{SR}^{calc}) of the SRT temperatures and their variation with pressure for the series of pseudo-ternaries $(Er_xR_{1-x})_2Fe_{14}B$.

Compound	T_{SR}^{exp} (K)	T_{SR}^{calc} (K)	dT_{SR}^{exp}/dp (K GPa^{-1})	dT_{SR}^{calc}/dp (K GPa^{-1})
$Er_2Fe_{14}B$	322	322	-20	-20
$(Er_{0.8}Y_{0.2})_2Fe_{14}B$	292	295	-20	-20 ± 2
$(Er_{0.6}Y_{0.4})_2Fe_{14}B$	254	256	-20	-20 ± 2
$(Er_{0.4}Y_{0.6})_2Fe_{14}B$	215	204	-20	-20 ± 2
$(Er_{0.2}Y_{0.8})_2Fe_{14}B$	143	125	-20	-20 ± 2
$(Er_{0.8}Gd_{0.2})_2Fe_{14}B$	306	303	-20	-20 ± 1
$(Er_{0.6}Gd_{0.4})_2Fe_{14}B$	284	276	-22.6	-20 ± 1
$(Er_{0.4}Gd_{0.6})_2Fe_{14}B$	253	237	-17.5	-20 ± 1
$(Er_{0.2}Gd_{0.8})_2Fe_{14}B$	194	168	-16.5	-20 ± 1
$(Er_{0.9}Dy_{0.1})_2Fe_{14}B$	235	235	-18	-18
$(Er_{0.8}Dy_{0.2})_2Fe_{14}B$	181	177	-14	-14
$(Er_{0.7}Dy_{0.3})_2Fe_{14}B$	130	128	-7	-7

2.1. Pseudo-ternary compounds with isotropic ions ($R \equiv Y$ and Gd)

The variation in the anisotropic properties due to the substitution of Er by either Y or Gd should be similar in both series of compounds. We have investigated these compounds in order to elucidate the influence of the pressure on the exchange interaction. This point is indeed very important in our study because not only the CEF interaction and Fe sublattice anisotropy are relevant in driving the SRT phenomena but also the R–Fe exchange interaction plays an important role. In these pseudo-ternary compounds, three kinds of exchange interaction should be clearly distinguished.

(i) The iron intersublattice exchange interaction $\mathcal{I}_{Fe-Fe}$ is responsible for the magnetic order and causes strong magnetovolume effects in these compounds.

(ii) The exchange interaction $\mathcal{I}_{R-R'}$ between the rare-earth magnetic sublattices as well as the intrasublattice rare-earth exchange interaction $\mathcal{I}_{R-R}$ has its origin in the indirect RKKY mechanism. As a consequence it is very weak and is usually considered negligible in such compounds.
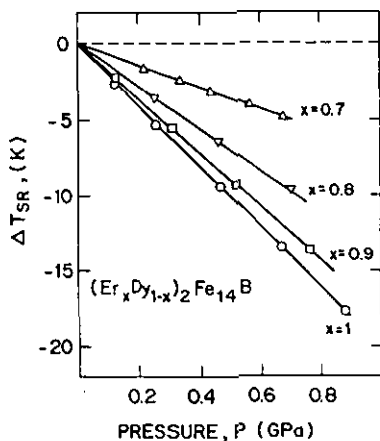
Figure 3. The shifts of T_{SR} as a function of the hydrostatic pressure for the $(Er_x Dy_{1-x})_2 Fe_{14}B$ series of compounds.
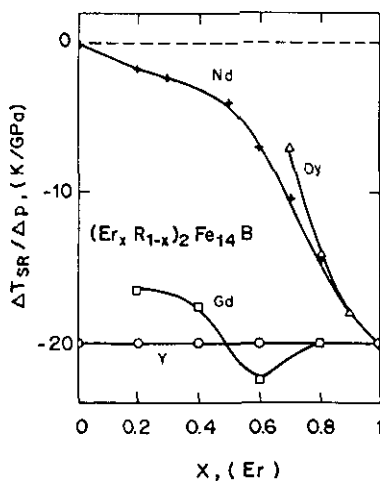

Figure 4. Dependence of $\Delta T_{SR}/\Delta p$ on the R content for different $(Er_x R_{1-x})_2 Fe_{14}B$ series of compounds: O, Y; □, Gd; Δ, Dy; +, Nd; ——, guides for the eye.

(iii) The intersublattice 4f–3d exchange interactions $\mathcal{I}_{R-Fe}$ and $\mathcal{I}_{R'-Fe}$ are, from the viewpoint of the study of the SRT phenomena, the most important contributions to the overall exchange interaction. These interactions initially were assumed by Campbell (1972) to take place through the exchange interaction between 4f and 5d electrons. Recently Belorizky *et al* (1987) have pointed out that the $\mathcal{I}_{R-Fe}$ strength is characteristic of the rare-earth ion. Brooks *et al* (1991) and Li *et al* (1991) gained a deeper insight into this subject, confirming in all cases that the Campbell hypothesis was correct.

In the case of $(Er_x Y_{1-x})_2 Fe_{14}B$ we have a similar $\mathcal{I}_{Fe-Fe}$ interaction for all the compounds along the series. However, $\mathcal{I}_{R-Fe}$ drastically changes within the series,

going from a non-zero value of $\mathcal{I}_{Er-Fe}$ to $\mathcal{I}_{Y-Fe} = 0$. For the (Er$_x$Gd$_{1-x}$)$_2$Fe$_{14}$B series, the variation in the strength from $\mathcal{I}_{Er-Fe}$ to $\mathcal{I}_{Gd-Fe}$ is very small (Belorizky *et al* 1987). In spite of the large difference in the intensity of $\mathcal{I}_{R'-Fe}$ for both (R' $\equiv$ Y and Gd) series of compounds, we obtained a similar effect of the pressure on T_{SR} ($\Delta T_{SR}/\Delta p \simeq -20$ K GPa^{-1} (figure 4)). This constitutes a clear indication of the small influence of the pressure on the $\mathcal{I}_{R-Fe}$ exchange interaction. This result will become very important in the course of our research regarding rare-earth substituted intermetallics under pressure. On the one hand, it demonstrates that $\mathcal{I}_{R-Fe}$ should be very localized at the R sites, confirming the Campbell hypothesis. On the other hand it allows one to give a description of the observed anisotropic behaviour under pressure on the basis of the pressure dependence of the CEF interaction.

In figure 1 and table 1 we collect the T_{SR} obtained for both series of compounds. As we have already mentioned, the SRT determined for a compound originates in the interplay of the 3d and 4f anisotropies. As we increase the Y or Gd concentration, we produce a weakening of the Er sublattice anisotropy in the mixed compounds, whereas the 3d sublattice contribution remains, in principle, constant. As a consequence we observed a decrease in the T_{SR} in both series. We should expect in both series a similar decrease in T_{SR} with increasing Y or Gd concentration; however, we observed that this decrease is larger for the Er-Y than for the Er–Gd series. This result constitutes an indication that the 3d sublattice anisotropic behaviours are different in both series. This finding is in close agreement with the results obtained by Bolzoni *et al* (1987) who detected that the 3d sublattice anisotropy is substantially higher for Y$_2$Fe$_{14}$B than for Gd$_2$Fe$_{14}$B ($K_1^{Gd_2Fe_{14}B} = 0.6K_1^{Y_2Fe_{14}B}$, where K_1 is the first anisotropy constant).

The SRT for Er$_2$Fe$_{14}$B from axis to plane is very sharp. Some experimental and theoretical results (Ibarra *et al* 1992b, Piquè *et al* 1992a, b) indicated that it is a first-order phase transition. In order to elucidate the nature of this transition, we measured the polar dependence of $M_\parallel$ and $M_\perp$. From these measurements we determined the EMDs at several temperatures. From the results obtained, we can conclude that even for a very low Er concentration ($x = 0.2$) the SRT takes place from the c-axis to the basal plane. In figure 5 we represent the results obtained for (Er$_{0.2}$Y$_{0.8}$)$_2$Fe$_{14}$B where the change in the sign of the slope of $M_\perp$ in the c axis direction indicates that this direction, which is the EMD above 130 K, becomes the hard magnetization direction below 125 K. The change in the sign of the slope of $M_\perp$ at $\pi/2$, which is a direction in the basal plane, shows that at 125 K the EMD lies on it. We did not find any temperature at which the system presents an easy cone magnetic structure. These results are in good agreement with torque measurements performed on (Er$_{0.1}$Y$_{0.9}$)$_2$Fe$_{14}$B (Koon *et al* 1991) in which a very sharp transition was observed even at this very low Er concentration.

The behaviour of (Er$_{0.2}$Gd$_{0.8}$)$_2$Fe$_{14}$B in the T_{SR} region is different from that of the (Er$_{0.2}$Y$_{0.8}$)$_2$Fe$_{14}$B compound. Measurements of the polar dependence of $M_\perp$ performed on a magnetically aligned sample of this compound are shown in figure 6. From these measurements it is clear that the SRT from axis to plane takes place in a range of temperatures of about 20 K and in this temperature range the system evolves through an intermediate conical magnetic structure (see figure 6(b)). This behaviour is an indication that the 3d sublattice anisotropy energy in the Gd–Er–Fe–B system cannot be merely expressed in terms of K_1. Bolzoni *et al* (1987) attributed the origin of the 3d sublattice anisotropy in R$_2$Fe$_{14}$B to the competition between the contributions for the different 3d sites. Under such a hypothesis they
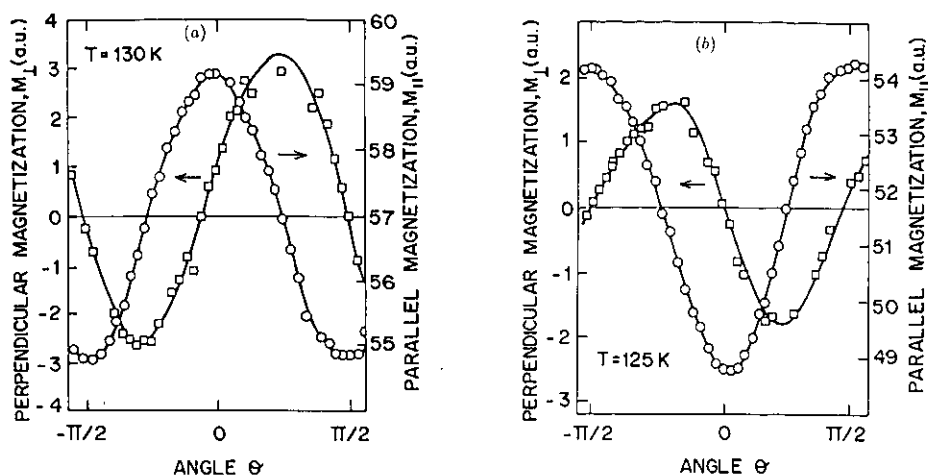
Figure 5. Polar plots of the parallel component $M_\parallel$ (O) and perpendicular component $M_\perp$ ($\square$) of the magnetization for an applied magnetic field of 1 kOe for the $(Er_{0.2}Y_{0.8})_2Fe_{14}B$ compound (a.u., arbitrary units): (a) at 130 K; (b) at 125 K.

explained the different values of K_1 for $Y_2Fe_{14}B$ and $Gd_2Fe_{14}B$. The behaviour observed for the Er–Gd series cannot be explained within this picture, indicating that some other interactions should be taken into account. An anisotropic character of the 5d–3d exchange interaction in $Gd_2Fe_{14}B$ could be possible. A similar hypothesis was successfully considered by Ballou *et al* (1987) in order to explain the different anisotropy energies of $GdCo_5$ and YCo_5. They pointed out that such an anisotropy could arise from preferential orbital hybridization of the 3d–5d bands. The existence of such an anisotropy in the exchange interaction involving 5d band electrons would give rise to an effective second anisotropy constant $K_2 < 0$ (Ballou *et al* 1987) and consequently this additional contribution to the overall anisotropy energy could be in the origin of the conical magnetic structure observed for $(Er_xGd_{1-x})_2Fe_{14}B$. This anisotropy in the 3d–5d exchange interaction could also be the origin of the peculiar behaviour observed in the variation in T_{SR} under pressure for the Er–Gd compounds as is possible to observe in figure 4.

2.2. Pseudo-ternary compounds with anisotropic ions ($R' \equiv Dy$ and Nd)

The anisotropic zero-pressure behaviour of these compounds has been extensively studied (Niarchos and Simopoulos 1986, Boltich *et al* 1987, Rechenberg *et al* 1987, del Moral *et al* 1988, 1989, Ibarra *et al* 1988, 1989, Marusi *et al* 1990). The purpose of the present research is to study the influence of applied pressure on such a behaviour. We have taken, as a reference probe for such a study, the change in T_{SR} under pressure. These compounds are characterized by a rich magnetic phase diagram, mainly in the Nd–Er series. In the case of $(Er_xDy_{1-x})_2Fe_{14}B$ the SRT (axis–cone) is basically driven by competing second-order CEF terms, being quite sensitive to the pressure. In the case of the $(Er_xNd_{1-x})_2Fe_{14}B$ series, not only the axis–cone 1 but also a cone 1–cone 2 SRT was observed at low temperatures (Ibarra *et al* 1988, del Moral *et al* 1989). This new kind of spontaneous SRT has recently been explained by Cadogan and Li (1992). In the course of the present investigation we
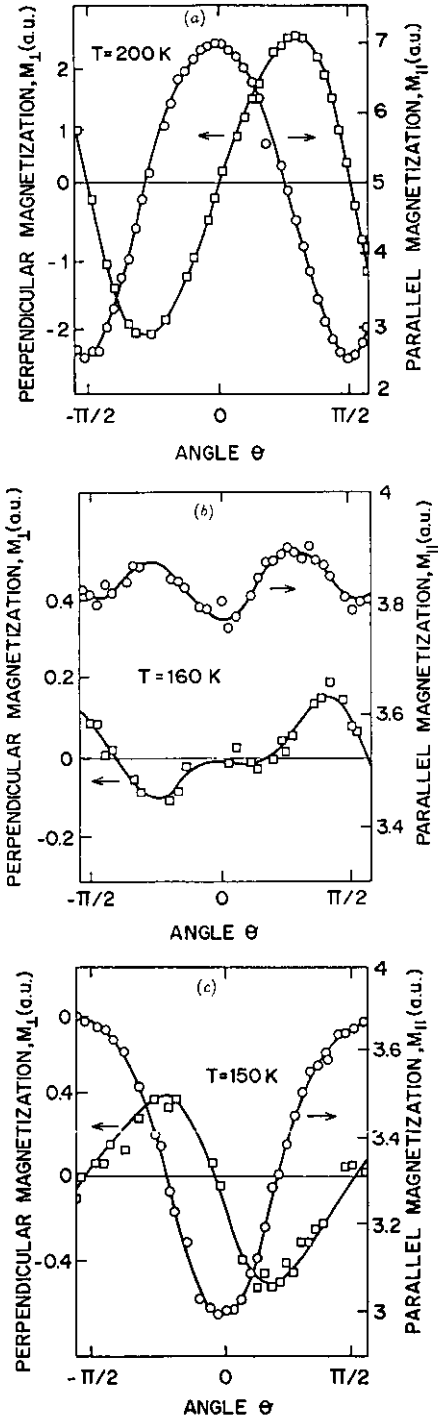
Figure 6. Polar plots of the parallel component $M_{||}$ (○) and perpendicular component $M_\perp$ (□) of the magnetization for an applied magnetic field of 1 kOe for the $(Er_{0.2}Gd_{0.8})_2Fe_{14}B$ compound (a.u., arbitrary units): (*a*) at 200 K; (*b*) at 160 K; (*c*) at 150 K.

have determined the variation with pressure in the axis–cone T_{SR}. In figure 4 we can observe that $\Delta T_{SR}/\Delta p$ drastically decreases for high Nd concentrations and, in fact, no variation in T_{SR} has been observed for $Nd_2Fe_{14}B$ up to 1 GPa (Kamarad *et al* 1987). Because the SRT of this compound is basically driven by high-order CEF terms, we are induced to conclude that the contributions of high-order terms (greater than the second-order quadrupolar term) to the CEF are not sensitive to the applied pressure. This conclusion is likely to be confirmed from experiments performed in the series $(Er_xHo_{1-x})_2Fe_{14}B$ (Ibarra *et al* 1992b) and $RFe_{10}V_2$ (Arnold *et al* 1992). The compound $(Er_{0.3}Ho_{0.7})_2Fe_{14}B$, as was observed in $(Er_{0.3}Nd_{0.7})_2Fe_{14}B$, presents two well defined peak anomalies in the AC initial magnetic susceptibility at $T_{SR1} = 80$ K and $T_{SR2} = 36$ K. These anomalies have been associated with an axis–cone 1 and a cone 1–cone 2 SRT, respectively, (Ibarra *et al* 1992b). This last SRT is mainly caused by high-order CEF and, as can be seen in figure 7, is completely pressure independent up to 0.74 GPa. A similar behaviour has been recently found in the study of the SRT phenomena of $RFe_{10}V_2$ ($R \equiv$ Nd, Dy and Er) compounds, in which the SRTs are driven by high-order CEF terms (Algarabel and Ibarra 1988) and no pressure effect was observed on the SRT temperature (Arnold *et al* 1992).
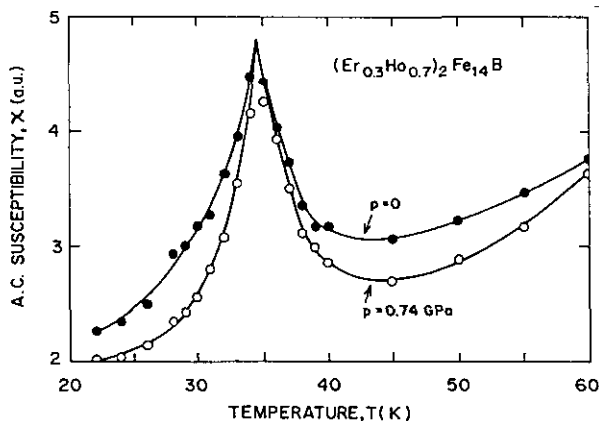

Figure 7. Thermal dependence of the AC initial magnetic susceptibility for $(Er_{0.3}Ho_{0.7})_2Fe_{14}B$ (a.u., arbitrary units): ●, at atmospheric pressure; ○, under a pressure of 0.74 GPa. The peak-like anomalies correspond to the cone 1–cone 2 SRT (see text).

3. Theoretical model

In order to account for the anisotropic behaviour observed in the pseudo-ternary $(Er_xR'_{1-x})Fe_{14}B$ compounds under pressure, we shall consider a model based on a single-ion origin for the anisotropy of the R ion, described as usual, within the Stevens operator formalism, together with the mean-field approximation to describe the $\mathcal{I}_{R-Fe}$

exchange interaction. This model, which also takes into account the non-collinearity between the different magnetic sublattices during the SRT, has been successfully used to account for the thermal dependence of the SRT angle in the $Pr_xNd_{1-x}Co_5$ series (Ibarra *et al* 1991) and also recently in the $(Er_xHo_{1-x})_2Fe_{14}B$ series (Ibarra *et al* 1992b), where a more detailed explanation of the model is given.

The CEF Hamiltonian compatible with the orthorhombic point symmetry has been considered up to fourth order for each rare-earth ion R, as

$$H_{CEF}^R = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0. \tag{1}$$

Owing to the S state of the Gd and Y ions this contribution does not exist. The exchange interaction is described by the Hamiltonian

$$H_{ex}^R = g_J \mu_B H_{mol}(J_z \cos\theta + J_x \sin\theta) \tag{2}$$

where H_{mol} is the molecular field which describes the $\mathcal{I}_{R-Fe}$ exchange interaction, g_J is the Landé factor for the multiplet J, J_z and J_x are the angular momentum operators associated with the R^{3+} ion and θ is the angle that μ_{Fe} makes with the c axis.

The rare-earth ion contribution to the free energy $F_R(\theta, T)$ is obtained as usual from the eigenvalues and eigenvectors of Hamiltonian $H^R = H_{CEF}^R + H_{Ex}^R$, through the partition function $Z_R(\theta, T)$ for each ion:

$$F(\theta, T) = x F_{Er}(\theta, T) + (1-x) F_{R'}(\theta, T) \tag{3}$$

where

$$F_R = -k_B T \ln[Z_R(\theta, T)]. \tag{4}$$

The free energy for the iron sublattice was obtained by replacing the Fe sublattice magnetic anisotropy by the anisotropy measured in the compound $Y_2Fe_{14}B$, i.e. $F_{Fe}(\theta, T) = K_1(T) \sin^2\theta$. The overall free energy $F_T(\theta, T)$ becomes

$$F_T(\theta, T) = F(\theta, T) + K_1(T) \sin^2\theta. \tag{5}$$

In the case of the $(Er_xGd_{1-x})_2Fe_{14}B$ series the Fe sublattice first-order anisotropy constant K_1^{Er-Gd} has been linearly interpolated with concentration x between the different values observed for $Y_2Fe_{14}B$ and $Gd_2Fe_{14}B$ (Bolzoni *et al* 1987):

$$K_1^{Er-Gd} \equiv x K_1^Y + (1-x) K_1^{Gd}. \tag{6}$$

The CEF parameters used for Er are the same as those that we used to describe the SRT in the Er–Dy and Er–Ho series (table 2). The theoretical fits of T_{SR} and $\Delta T_{SR}/\Delta p$ achieved for the different series are quite good, as can be seen in figure 8. The theoretical results show that the axis–plane transition should take place quite sharply for both series of compounds as shown in figure 9 for Er–Y. The calculation of $\Delta T_{SR}/\Delta p$ was done by introducing the effect of the pressure on the CEF parameters $\Delta B_2^0/\Delta p$ in the Hamiltonian (1). We started from the values at zero pressure (Ibarra *et al* 1989) (table 2) to reproduce the experimental values of T_{SR} at a determined pressure. From these results we could obtain $\Delta B_2^0/\Delta p$ which closely fits the experiment using the values $\Delta B_2^0/\Delta p = 0.06$ K GPa^{-1} for Er^{3+} and $\Delta B_0^2/\Delta p = 0.13$ K GPa^{-1} for Dy^{3+} ions (see table 2).
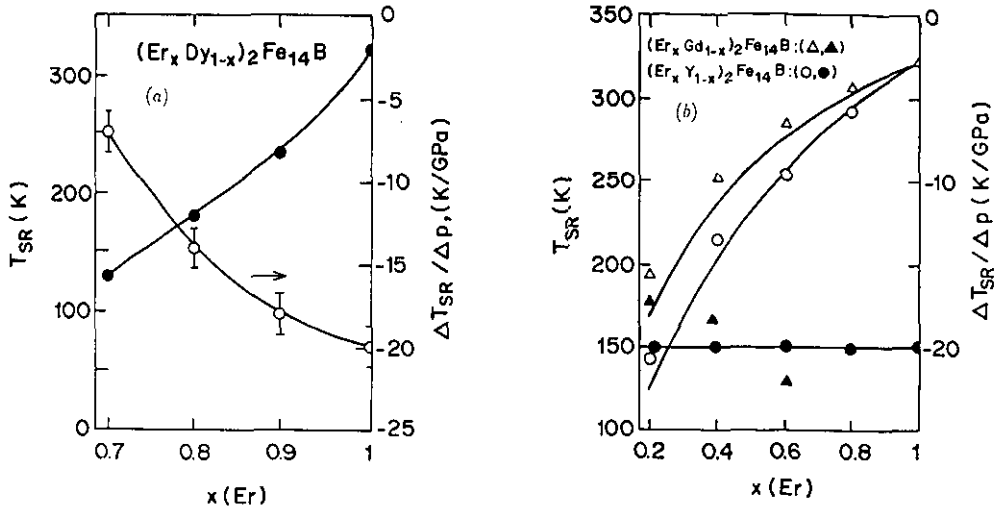
Figure 8. Dependence of the T_{SR} (O, $\triangle$) and its variation with pressure ($\bullet$, $\blacktriangle$) for the $(Er_x R_{1-x})_2 Fe_{14}B$ series with (a) R $\equiv$ Dy (O, $\bullet$), (b) R $\equiv$ Gd ($\triangle$, $\blacktriangle$) and R $\equiv$ Y (O, $\bullet$); ——, theoretical fits.
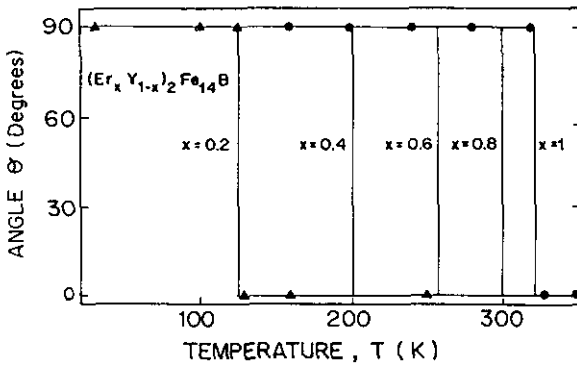

Figure 9. Thermal evolution of the spin reorientation angle in the $(Er_x Y_{1-x})_2 Fe_{14}B$ series: $\bullet$, experimental results (Hirosawa *et al* 1986); $\triangle$, this work; ——, theoretical fits.

Table 2. Values of the CEF parameter B_n^m and the exchange energy $2\mu_B H_{ex}$ for the Er^{3+} and Dy^{3+} ions in the $R_2 Fe_{14}B$ compounds, as well as the variation $\Delta B_2^0 / \Delta p$ in B_2^0 with pressure.

Ion	B_2^0 (K)	B_2^2 (K)	B_4^0 (K)	$2\mu_B H_{ex}$ (K)	$\Delta B_2^0 / \Delta p$ (K GPa^{-1})
Er^{3+}	0.3	-0.27	-0.0006	375	0.06
Dy^{3+}	-0.9 ± 0.05	0.57	0.002	375	0.13 ± 0.03

4. Conclusions

In the present paper we summarize a substantial amount of experimental and theoretical work carried out on the series of pseudo-ternary compounds $(Er_xR_{1-x})_2Fe_{14}B$ (R $\equiv$ Nd, Dy, Gd and Y) concerning the SRT behaviour. From these studies we can conclude the following.

(i) In the absence of a single crystal, measurements of the AC magnetic susceptibility and magnetization (i.e. polar dependence of $M_{\parallel}$ and $M_{\perp}$) on magnetically aligned samples can give fully reliable information on the parameters which drive the basic interaction in rare-earth intermetallics. These kinds of study can be undertaken for rare-earth intermetallic compounds which present magnetic order and high uniaxial anisotropy at room temperature and also competing anisotropies between the different magnetic sublattices. The study of SRT processes and T_{SR} in polycrystalline substituted rare-earth intermetallic compounds is a suitable tool for obtaining realistic values for the CEF and exchange parameters.

(ii) From the comparison of the zero-pressure anisotropic behaviour between the $(Er_xY_{1-x})_2Fe_{14}B$ and $(Er_xGd_{1-x})_2Fe_{14}B$ series the possible anisotropic character of the $\mathcal{I}_{R-Fe}$ exchange interaction is concluded.

(iii) The variation in T_{SR} with concentration in these series can be understood by using a single-ion non-collinear mean-field model, where the value for the 3d magnetic sublattice anisotropy energy in $Y_2Fe_{14}B$ and $Gd_2Fe_{14}B$ is taken into account, through its phenomenological expression.

(iv) The present work, as far as we know, constitutes the first systematic attempt to study the influence of the pressure on the CEF in rare-earth intermetallics. For such a purpose we have studied the dependence of T_{SR} on hydrostatic pressure. The observed effect is quite large, ranging up to -20 K GPa^{-1} for $Er_2Fe_{14}B$.

(v) From the analysis of the experimental results, it is definitely concluded that the $\mathcal{I}_{R-Fe}$ exchange interaction is not affected by the pressure, providing evidence of the localized character of this interaction. It is also found that high-order CEF terms greater than quadrupolar are not sensitive to the pressure. Under such an assumption the anisotropic behaviour under pressure is well explained, which leads to a determination of the variation in B_2^0 under pressure.

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