Spin-Reorientation and Magnetostriction in Highly Oriented (Er$_{1-x}$Tb$_x$)$_2$Fe$_{14}$B

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(Received; May 1, 1998, Accepted; August 26, 1998)

Magnetostriction measurements in highly-oriented ribbons of (Er$_{1-x}$Tb$_x$)$_2$Fe$_{14}$B with $0 \leq x \leq 0.45$, fabricated by a rapid-quenching method have been performed in order to investigate the lattice deformation at the spin reorientation (SR) transitions. The c-axis of the tetragonal cell was found to be aligned perpendicular to the ribbon surface. The sum of the longitudinal and transverse magnetostriction $\lambda_L + \lambda_T$, with fields applied within the ribbon plane, took a maximum at successive SR temperatures. A model calculation of the volume change $\Delta V/V$ was made by assuming that only the crystalline electric field (CEF) potentials at Er and Tb sites affect the volume change. This calculation showed that $\Delta V/V$ exhibits a sharp peak at SR temperatures, which is in accordance with the experimental peaks of $\lambda_L + \lambda_T$.

**Key words**: magnetostriction, spin reorientation, crystalline electric field, Nd$_2$Fe$_{14}$B, rapid-quenching method

1. Introduction

Magnetic properties of $R_2$Fe$_{14}$B ($R$: rare earth element) have been extensively studied, in connection with the high-performance Nd-Fe-B permanent magnets. In this system, an interplay among the $R$-Fe exchange interaction, CEF potential acting on $R$ ions, and a large magnetic moment of the Fe sublattice leads to a variety of magnetic properties such as first-order magnetization process (FOMP) and SR transitions. In the case of Er$_2$Fe$_{14}$B, an abrupt SR transition at $T_{SR} = 323$ K was observed, above which the direction of the magnetic moments changes to the tetragonal [001] from [100]. Partial replacement of Tb for Er is known to cause a rapid decrease of $T_{SR}$ and an appearance of an intermediate phase with the tilted easy axis. Such a behavior can be understood qualitatively by the competing magnetic anisotropy arising from the Er, Tb, and Fe sublattices. That is, Er favors the easy [100] direction, while Tb and Fe tend to align along the [001].

In general, such SR transitions will be accompanied by a considerable lattice deformation, since there is a large orbital contribution to the $R$ magnetic moments, resulting in a strong coupling between spin and lattice systems. It is therefore of interest to investigate the magnetoelastic properties of this mixed system, because not only the SR occurs around the room temperature, but also $T_{SR}$ can be controlled by changing the Tb content. In this paper, we report the structural and magnetoelastic studies in rapidly-quenched (Er$_{1-x}$Tb$_x$)$_2$Fe$_{14}$B ribbons, which exhibited a significant crystallite orientation. Model calculations of volume expansion have also been done in order to analyze the experiments.

2. Experimental

Ribbon samples of (Er$_{1-x}$Tb$_x$)$_2$Fe$_{14}$B with $0 \leq x \leq 0.45$ were prepared by a single-roller rapidly-quenching method in an Ar atmosphere. A surface velocity of the copper wheel (15 cm diameter) was varied between $V_s = 4 \sim 31$ m/s, ejection pressure of Ar gas $P_{Ar} = 0.6 \sim 1.4$ kg/cm$^2$, and the orifice diameter of the quartz crucible was fixed to 0.5 mm. Thickness of the ribbon was about 30 μm for $V_s = 15.7$ m/s. Compositions were checked by an ICP analysis. Magnetostriction measurements were performed by a capacitance method apparatus, by which we observed the $\Delta l/l$.

![Fig. 1 X-ray diffraction patterns for Er$_2$Fe$_{14}$B ribbons quenched with wheel velocity $V_s = 15.7$ m/s, showing those of the free side, wheel side and the center portion of the ribbon.](image1)

![Fig. 2 Intensity ratio I(006) / I(410) as obtained from X-ray measurements, (a) as a function of wheel velocity $V_s$ for Er$_2$Fe$_{14}$B, and (b) as a function of Tb content $x$ for (Er$_{1-x}$Tb$_x$)$_2$Fe$_{14}$B.](image2)
parallel ($\lambda_{\|}$) and perpendicular ($\lambda_{\perp}$) to the field direction within the ribbon plane.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of Er$_2$Fe$_4$B ribbons. Patterns of free-side, wheel-side, and the center portion of the ribbon flakes, the latter of which was exposed by chemical etching, are separately given in order to evaluate the degree of alignment in each portion. For the free-side surface, almost only the (00l)-type reflections were observed, while small peaks of other type of reflections such as (410) were additionally noticed at the wheel side and center portion. These results therefore suggest that the $c$-axis of the tetragonal cell aligns perpendicular to the ribbon surface. Similar preferential crystallite orientation has been reported for Nd-Fe-B rapid-quenched ribbons [9]. In order to optimize the degree of alignment, we have adjusted the wheel velocity $V_4$ and ejection pressure of Ar gas $P_4$. Figure 2(a) shows the intensity ratio of (006) and (410) reflections as a function of $V_4$ with different values of $P_4$ for the free-side surface of Er$_2$Fe$_4$B ribbons. This data revealed that the $V_4 = 15.7$ m/s and $P_4 = 0.6$ kg/cm$^2$ is the optimum condition. Effect of Tb content on the alignment was investigated as shown in Fig. 2(b), which has demonstrated a similarly good alignment in the (Er$_{1-x}$Tb$_x$)$_2$Fe$_4$B ribbons. In order to estimate the bulk averages of the alignment, we have measured the magnetization curves with fields parallel and perpendicular to the ribbon surface, which have shown that the full width at half maximum of the $c$-axis orientation distribution is 12$^\circ$ ± 5$^\circ$. We have then measured the magnetization as functions of field and temperature. These experiments have shown that $T_{SR} = 319$ K for the $x = 0$ sample, which is in good agreement with literature values [4,6].

Next we measured the longitudinal and transverse magnetostriiction constants $\lambda_{\|}$ and $\lambda_{\perp}$ as a function of magnetic field at fixed temperatures. Examples of the results are shown in Fig. 3, in which the sum of the longitudinal and transverse magnetostriiction $\lambda_{\|} + \lambda_{\perp}$ is plotted against temperature. From Figs. 3(a) and 3(b) one can see that overall values of $\lambda_{\|} + \lambda_{\perp}$ increase with increasing field. Such a behavior is consistent with the report by Algarabel [10] and suggests the contribution from the volume magnetostriiction owing mainly to the Fe 3d bond. The most significant feature in Fig. 3(a) is a maximum of $\lambda_{\|} + \lambda_{\perp}$ around 325 K. This temperature of maximum slightly increases with increasing field. It must be noted that the anisotropic magnetostriiction $\lambda_{\|} - \lambda_{\perp}$ is almost constant in this temperature and field range. Since the observed peak temperature of $\lambda_{\|} + \lambda_{\perp}$ almost coincides to $T_{SR}$ of the $x = 0$ sample, we can interpret the phenomena as the areal increase of the $c$-plane at the SR transition, suppose that the alignment is perfect. The $x = 0.106$ sample, on the other hand, exhibits a double peak at $T_1 = 210$ K and $T_2 = 145$ K. Lim et al. [9] reported such successive transitions in (Er$_{1-x}$Tb$_x$)$_2$Fe$_4$B with 0.05 $\leq$ $x$ $\leq$ 0.15 in the similar temperature range and explained the higher and lower transitions as the SR's from axial to tilted, and tilted to planar phases. Observed double peak, therefore, appears to correspond the areal increase of the $c$-plane at the beginning and closing of the easy-axis rotation, that is, the two SR transitions.

Fig. 3 Temperature dependence of the areal magnetostriiction $\lambda_{\|} + \lambda_{\perp}$ in (Er$_{1-x}$Tb$_x$)$_2$Fe$_4$B with (a) $x = 0$, and (b) $x = 0.106$. The field was applied within the ribbon plane. The solid lines are guides for the eye.

Fig. 4 Calculated temperature dependence of the easy-axis direction $\theta$, and volume change $\Delta V/V$ in (Er$_{1-x}$Tb$_x$)$_2$Fe$_4$B with (a) $x = 0$, and (b) $x = 0.106$. The field is applied in the [100] direction ($\theta = 90^\circ$).
Fig. 5 Field dependence of calculated peak temperatures of $\Delta V/V$ (solid and dashed lines), and observed peak temperatures of $\lambda_\parallel + \lambda_\perp$ (solid circles) in (Er$_{1-x}$Tb$_x$)$_2$Fe$_{14}$B.

In order to analyze the experimental data above, we have made a model calculation of volume magnetostriction arising from CEF potential of Er and Tb sites. First we assume that the total free energy of (Er$_{1-x}$Tb$_x$)$_2$Fe$_{14}$B is given by

$$F(H, T) = (1 - x)F_{Er} + xF_{Tb} + E_{Fe} + C(\Delta V/V_0)^2.$$  \hspace{1cm} (1)

where the first three terms are essentially the same as those given by Eq. (1) in Ref. 7, and respectively express the (magnetic) free energy for Er, Tb, and Fe sublattices. The last term denotes an elastic energy for the volume change $\Delta V/V_0$, in which the constant $C$ is fixed to be $2.0 \times 10^9$ K by adopting the bulk modulus value reported for Er$_2$Fe$_{14}$B (11). As for the CEF Hamiltonian for the Er and Tb sites, we simply assumed that (i) only the axial CEF coefficients $A_{2u}^0$, $A_{4u}^0$, and $A_{6u}^0$ are modified by the volume change, and (ii) the volume dependence of $A_{2u}^0$ is determined by the point charge approximation. The latter assumption directly leads to the following relations:

$$A_{2u}^0(V) = A_{2u}^0(V_0) G_{2u}^0 \left[1 - \Delta V/V_0\right],$$

$$A_{4u}^0(V) = A_{4u}^0(V_0) G_{4u}^0 \left[1 - (5/3)\Delta V/V_0\right],$$

$$A_{6u}^0(V) = A_{6u}^0(V_0) G_{6u}^0 \left[1 - (7/3)\Delta V/V_0\right],$$  \hspace{1cm} (2)

where $V = V_0 + \Delta V$, and $G_{2u}^0, G_{4u}^0, G_{6u}^0$ should be equal to unity if the expansion is isotropic. On condition that the total free energy of Eq. (1) takes a minimum, we have simultaneously calculated $\Delta V/V = \Delta V/V_0$, and the magnitude and direction of magnetic moments in each sublattice for various temperature and field values. The same values of CEF parameters $A_{2u}^n$, and molecular field $H_{CEF}$ were used as those given in Ref. 3, except that $A_{2u}^0$ for Er$_2$Fe$_{14}$B was reduced by 7% (283 K/tet-2) so as to best fit the observed $T_{QK}(x = 0)$ in the present sample. In the previous report (11) we simply set $G_{2u}^0 = 1$, and $G_{4u}^0 = G_{6u}^0 = 0$. This set of $G_{2u}^0$ gave us a reasonable agreement with the observation for $x = 0.106$. In the present study, by inspecting various sets of $G_{2u}^0$ values, we have found that, for smaller $x$, non-zero values of $G_{2u}^0$ and $G_{6u}^0$ gives better agreement with experiments. Here, we show the results for $G_{2u}^0 = 1$, $G_{4u}^0 = -1$, and $G_{6u}^0 = 1$.

Figure 4 shows the calculated easy-axis direction $\theta$ and the volume change $\Delta V/V$ as a function of temperature. For $x = 0$, as shown in Fig. 4(a), a discontinuous change of $\Delta V/V$ is seen at $T_{QK}$ for $H = 0$. With increasing the field strength, applied along the [001] direction, $T_{QK}$ increases and the anomalous change in $\Delta V/V$ around $T_{QK}$ become smaller. This result is in qualitative agreement with the experiments given in Fig. 3(a), although observed $\lambda_\parallel + \lambda_\perp$ does not show a discontinuous change but exhibits just a maximum. In the case of $x = 0.106$, calculated $\Delta V/V$ exhibit a double peak at $T_1$ and $T_2$. It should be noted that, with increasing field, the peak at $T_2$ just shifts to the higher values, whereas the $T_1$ peak becomes smeared which is similar to the result for $x = 0$. Such calculated results appears to correspond to the observation (Fig. 3(b)), although the field dependence of observed $T_{QK}$ peak is not obvious for the lack of data points. Calculated field dependence of the peak temperatures of $\Delta V/V$ ($T_{QK}$ for $x = 0$, $T_1$, and $T_2$ for $x = 0.106$) is shown in Fig. 5, together with the observed peak temperatures of $\lambda_\parallel + \lambda_\perp$. Although calculated peak temperatures exhibit a rather large increase with field, observed change is considerably small. The dashed lines in Fig. 5, on the other hand, are the calculated peak temperatures for the field applied along the [001] direction, which exhibit a rapid decrease with field. We therefore interpret the small field dependence of the observed peak temperature is owing to the incomplete c-axis alignment of the present ribbons.

In conclusion, we have shown that magnetostriction constants $\lambda_\parallel + \lambda_\perp$ take a maximum at successive SR transitions, and these peaks can be explained as the volume expansion owing to the CEF potential at $R$ sites.

Acknowledgements We are grateful to Professor Motohiko Yamada for his fruitful discussion about the model calculation of $\Delta V/V$. This work was partly supported by the Murata Science Foundation, a Grant-in-Aid for Scientific Research (No. 09650002) from the Ministry of Education, Science, Sports and Culture, and also by the Mazda Foundation.

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