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Citation: Appl. Phys. Lett. 112, 162405 (2018); doi: 10.1063/1.5018875
View online: https://doi.org/10.1063/1.5018875
View Table of Contents: http://aip.scitation.org/toc/apl/112/16
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Site-specific magnetic anisotropies in $R_2$Fe$_{14}$B systems

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(Received 11 December 2017; accepted 23 March 2018; published online 17 April 2018)

The local magnetic anisotropy of $R$ ions in $R_2$Fe$_{14}$B ($R = \text{Dy, Ho}$) systems is studied based on a microscopic effective spin model constructed from the information obtained by using first-principles calculations. By taking into account up to 6-th order crystal electric field parameters, the model satisfactorily describes the observed magnetization curves and the temperature dependence of anisotropy constants. We found that at low temperatures, the noncollinear structure appears in the Ho$_2$Fe$_{14}$B system reflecting the local magnetic anisotropy. Published by AIP Publishing. https://doi.org/10.1063/1.5018875

Understanding the coercivity mechanisms of rare-earth-based permanent magnets is crucially important for renewable and sustainable development in engineering.$^{1,2}$ In research on magnetic materials, the coercivity of permanent magnets is usually described by the phenomenological formula $H_c(T) = zH_A(T) - N_{eff}M_s(T)$, which was proposed by Kronmüller et al.,$^3$ where $H_c(T)$ and $H_A(T)$ are the coercive and the magnetocrystalline anisotropy (MA) field, respectively. $M_s(T)$ is the saturation magnetization, $N_{eff}$ ($\geq 0$) is the effective demagnetization factor, and $z$ ($\leq 1$) is the reduction in $H_A(T)$ due to structural inhomogeneities. In particular, the first term on the right-hand side of the formula gives the intrinsic effect of the material on its coercivity.

Recent studies of Nd–Fe–B magnets have shown that the magnetic properties at finite temperatures are obtained from the free energies of the partial system for each $R$ ion, which is based on the first-principles method. We confirm that the magnetization curves are satisfactorily reproduced by this model by performing equilibrium calculations. Note that $R$ ions around the intergranular phases can be easily incorporated into the effective spin model.

It is well known that the magnetizations of Nd$_2$Fe$_{14}$B and Ho$_2$Fe$_{14}$B are tilted from the $c$ axis at $T = 0$ (K).$^{15,16}$ The tilt angle decreases with increasing temperature and vanishes at 135 and 58 K, respectively. This phenomenon is called the spin reorientation transition (SRT). The tilt angle vanishes discontinuously for $R = \text{Er, Tm,}$ and Yb.$^{17}$ On the other hand, the SRT does not occur for $R = \text{Pr and Dy.}$ It may be natural that the SRT is related to the local MA on the inequivalent $R$ sites, which is determined by the CEF. To clarify the role of the inequivalent $R$ sites in the MA, it may be desirable to calculate the CEF parameter values using first-principles.

To this end, we calculate the CEF parameter values using the first-principles method for Ho$_2$Fe$_{14}$B and Dy$_2$Fe$_{14}$B. These materials are appropriate for study of the SRT because one shows the SRT and the other does not. We then construct a microscopic spin model taking into account the site-specific MA of Ho and Dy ions and the exchange interactions between Ho and Fe and between Dy and Fe. We calculate the magnetic field and temperature dependence of the magnetization.

We show that the SRT of Ho$_2$Fe$_{14}$B is reproduced reasonably well and clarify the mechanism of the SRT by calculating the local MA energy of the inequivalent $R$ sites.

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The magnetic properties of $R_2$Fe$_{14}$B may be studied by adopting the following Hamiltonian for two formula units (f.u.)\textsuperscript{12}

$$H = \sum_{i=1}^{4} H^{f}_{\text{CEF}}(i) - 28m \cdot H,$$

$$H^{f}_{\text{CEF}}(i) = H^{f}_{\text{CEF}}(i) + \left[2(gJ - 1)H_m(i) + gJH\right] \cdot \mathbf{j}_i,$$

where $H^{f}_{\text{CEF}}(i)$ is the effective Hamiltonian for the $i$-th $R$ ($i = 1, 2, 3,$ and $4$ for $f_1$, $g_1$, $f_2$, and $g_2$, respectively), $H$ is the external magnetic field, $m$ is the magnetic moment per single Fe ion, $gJ$ is the Landé $g$ factor, $H_m(i)$ is the Fe molecular field acting on the spin component of the $i$-th $R$, and $\mathbf{j}_i$ is the lowest $J$ multiplet for the $i$-th $R$. The factor $28$ is the number of Fe per two f.u. The CEF Hamiltonian for 4f electrons, $H^{f}_{\text{CEF}}(i)$, is given by

$$H^{f}_{\text{CEF}}(i) = \sum_{l,m} A^{f}_{lm}(i) \langle r^l \rangle \Theta_l \bar{O}^m_l,$$

where $A^{f}_{lm}(i)$ is the CEF parameter for the $i$-th $R$ ion, $\Theta_l$ and $\bar{O}^m_l$ are the Stevens factor and Stevens operator, respectively.\textsuperscript{18,19}

The CEF parameters $A^{f}_{lm}(i) \langle r^l \rangle$ in Eq. (3) are calculated from the Coulomb potential for the 4f orbital using the open-core method,\textsuperscript{20-23} in which to avoid self-interaction of the localized 4f electrons, we treat the 4f states as atomic-like core states, where the resultant spin of the $R^{3+}$ ion is maximal and nonspherical part of the 4f electron density is set equal to zero. To obtain the Coulomb potential, we use the full-potential linearized augmented plane wave plus the local orbital method implemented in the WIEN2k code.\textsuperscript{26} The Kohn–Sham equations are solved within the generalized gradient approximation.

Diagonalizing Eq. (2), we obtain the free energy per two f.u. as

$$F = \sum_{i=1}^{4} f_{\text{loc}}(i) - 28m \cdot H,$$

$$f_{\text{loc}}(i) = -k_B T \ln Z(i),$$

$$Z(i) = \sum_n \exp \left[ -E_n(i)/k_B T \right],$$

where $f_{\text{loc}}(i)$ and $Z(i)$ are the local MA energy and partition function, respectively, for the partial system of the $i$-th $R$, and $E_n(i)$ is the $n$-th eigenvalue of $H^{f}_{\text{CEF}}(i)$. The magnetization per two f.u. is expressed as

$$M = \sum_{i=1}^{4} m_i(i) + 28m,$$

$$m_i(i) = -gJ \sum_{n} \langle i, n | J_i | i, n \rangle \exp \left[ -E_n(i)/k_B T \right] / Z(i),$$

where $m_i(i)$ is the magnetic moment of the $i$-th $R$ ion and $| i, n \rangle$ is the $n$-th eigenstate of the $i$-th $R$ ion. Because we focus on the competition between the CEF and $R$–Fe exchange field, we neglect the MA of the Fe sublattice. It is justified because the observed MA in $Y_2$Fe$_{14}$B has almost a constant value $K_1 \sim 1.2$ (K) per single Fe ion,\textsuperscript{16} which is relatively small compared with that of the Ho and Dy ions.

In this model, the direction of the external field is fixed in a selected direction (here, [001] or [110]), and we treat the Fe magnetic moment $m$ as an external parameter. The direction of $m$, which is antiparallel to $H_m$, is expressed using the polar coordinates $(\theta, \phi)$. By calculating Eqs. (4)–(8) for a given $(\theta, \phi)$, we obtain the angular dependence of the free energy. The equilibrium direction of $m$ is determined by the minimum point of the free energy of the whole system in Eq. (4), which is expressed as $(\theta_{eq}, \phi_{eq})$. The remaining parameters are the magnitudes of $m$ and $H_m$. We adopt the value of 31.4 (μJ / f.u.) observed in $Y_2$Fe$_{14}$B\textsuperscript{16} as the magnetic moments $|m|$ on the Fe sublattice in both Ho$_2$Fe$_{14}$B and Dy$_2$Fe$_{14}$B in Eq. (7). The molecular fields $H_m[f(g)]$ can be estimated by the first principles calculations according to the following formula: $H_m[f(g)] = \Delta E[f(g)]/4S_d$, where $S_d$ is the resultant spin angular momentum of 4f electrons according to the Hund rule and $\Delta E[f(g)]$ is the excitation energy by spin flip of $S_d$ on the $f(g)$ site. Here, we calculate the $\Delta E[f(g)]$ from the energy increase in a single unit cell by using the open core method, in which we can designate the direction of $S_d$ by arranging the 4f electrons on the $f(g)$ site. The results for Dy ions are $H_m(f) = 229$ (K) and $H_m(g) = 238$ (K), and for Ho ions, they are $H_m(f) = 213$ (K) and $H_m(g) = 221$ (K). The molecular fields for both $R$ = Dy and Ho were also experimentally estimated as $H_m = 187$ (K) by Hiroawa et al.\textsuperscript{16}

The calculated value of the CEF parameters on the $f_1$ and $g_1$ sites in $R_2$Fe$_{14}$B ($R$ = Dy and Ho) is shown in Table I. For the $f_2$ and $g_2$ sites, $A^{f}_{lm} \langle r^l \rangle$ has opposite signs for $m = -2$ and $m = -6$. Table I clearly shows that the difference between inequivalent sites appears in the CEF parameter values; however, $A^{f}_{lm} \langle r^l \rangle$ for $m = -2$ and $m = -6$ does not contribute to the MA for the entire system in Eq. (4) because of the tetragonal crystal structure.\textsuperscript{27} We note that the CEF parameter values for $m = 0$ are almost the same between the inequivalent $f_1$ and $g_1$ sites in each $R$ ion.

<table>
<thead>
<tr>
<th>$R$ site</th>
<th>$A^{f}_{1}(r^2)$</th>
<th>$A^{f}_{2}(r^2)$</th>
<th>$A^{f}_{3}(r^4)$</th>
<th>$A^{f}_{4}(r^4)$</th>
<th>$A^{f}_{5}(r^4)$</th>
<th>$A^{f}_{6}(r^4)$</th>
<th>$A^{f}_{7}(r^6)$</th>
<th>$A^{f}_{8}(r^6)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_1$</td>
<td>351</td>
<td>-836</td>
<td>-40.0</td>
<td>60.1</td>
<td>-117</td>
<td>-1.67</td>
<td>-3.46</td>
<td>-13.7</td>
</tr>
<tr>
<td>$g_1$</td>
<td>373</td>
<td>64.5</td>
<td>-40.3</td>
<td>-44.3</td>
<td>54.9</td>
<td>-1.38</td>
<td>2.43</td>
<td>-9.82</td>
</tr>
<tr>
<td>$f_1$</td>
<td>345</td>
<td>-823</td>
<td>-38.2</td>
<td>56.2</td>
<td>-111</td>
<td>-1.46</td>
<td>-2.89</td>
<td>-12.3</td>
</tr>
<tr>
<td>$g_1$</td>
<td>358</td>
<td>45.1</td>
<td>-38.3</td>
<td>-40.6</td>
<td>49.6</td>
<td>-1.22</td>
<td>2.10</td>
<td>-8.64</td>
</tr>
</tbody>
</table>
which indicates that the magnetization of Dy$_2$Fe$_{14}$Bi is
$H = 0$. The solid and broken lines are results calculated
using the molecular field $H_m$ determined by the experiment$^{16}$ and the present
study, respectively. Filled circles are experimental results.$^{12}$

Figure 1 shows the magnetization curves along the [001] and [110] axes for Dy$_2$Fe$_{14}$B and Ho$_2$Fe$_{14}$B. The solid and
broken lines are the calculated results from Eq. (7), and the
filled circles are the experimental ones. The agreement
between the theoretical and experimental results is satisfactory,
which may suggest the validity of the calculated values of the CEF parameters. The results show that the magnetization along the [110] direction is zero for Dy$_2$Fe$_{14}$B at $H = 0$, which indicates that the magnetization of Dy$_2$Fe$_{14}$B is aligned along the $c$ axis at $H = 0$. On the other hand, the magnetization along the [110] direction of Ho$_2$Fe$_{14}$B is finite even at $H = 0$, which may be interpreted in terms of tilting of the magnetization of Ho$_2$Fe$_{14}$B magnetization.

Figure 2 shows the temperature dependence of the tilt angle of the magnetization defined by Eq. (7) in Ho$_2$Fe$_{14}$B at $H = 0$. Because the calculated azimuthal angle of the magnetization is $45^\circ$ at all temperatures, the tilt angle is defined as the arctangent of the ratio of the [001] component to the [110] component of the magnetization. The solid and broken lines are calculated results, and the solid circles are experimental ones. The tilt angle at $T = 0$ (K) is approximately $18^\circ$. The calculated results are consistent with the experimental ones. We note that crystalline $K_f$Fe$_{14}$B has fourfold rotational symmetry, and the azimuthal angle of the magnetization can be $135^\circ$, $-135^\circ$, or $-45^\circ$.

The inset of Fig. 2 shows the temperature dependence of the MA constant $K_1$ of Ho$_2$Fe$_{14}$B. The calculated results show satisfactory agreement with the experimental ones. The temperature at which the sign inversion of $K_1$ occurs corresponds to the transition point of the SRT temperature.

Now, we investigate the local MA and clarify the role of inequivalent sites in the magnetic properties. Hereafter, we use the value $H_m = 187$ K estimated experimentally because differences in $H_m$ have little effect on the magnetic properties. We first show the dependence of the local MA energy defined by Eq. (5) on the $H_m$ direction at $H = 0$.

Figure 3 shows the local MA energy in Eq. (5) and the total MA energy per single $R$ ion at $H = 0$ in Eq. (4) as a function of the polar angle of the $H_m$ at $T = 0$ (K) and 300 (K) in Dy$_2$Fe$_{14}$B and Ho$_2$Fe$_{14}$B. The azimuthal angle of $H_m$ is fixed to $\phi = 45^\circ$ or $-135^\circ$, which gives the minimum value of the total MA energy at each $\theta$. By rotating $\phi$ by $90^\circ$, the total MA energy is invariant, while the local MA energies are interchanged between $f_1(g_1)$ and $f_2(g_2)$ sites. As shown in Fig. 3, the difference between the local MA on the inequivalent sites is apparent, which mainly originate from the huge difference in $A^{\mu}(r^i)$ for $m = -2$ and $-6$ to the total MA are canceled out by the tetragonal symmetry. The equilibrium state is determined by the minimum of the total MA energy with respect to the direction of $H_m$. In Fig. 3(c), the total anisotropy energy has minimum at $\theta = 19^\circ$, which indicates the stable direction of the Fe magnetic moment in Ho$_2$Fe$_{14}$B. We have confirmed that the occurrence of the SRT at low temperatures is almost
of the magnetic moment on the valent value of the local MA. The relatively large deviation noncollinear magnetic structure appears owing to the inequivalent to the Fe magnetic moment; however, a small shown in Fig. 4. The magnetic moment
moments are forced to align by the strong R
including up to the 6-th order CEF parameters. The
nomenon is explained well in terms of the MA of
R
C21
Fe is mere 4


FIG. 4. Direction of magnetic moment on inequivalent R and Fe ions in H0.5Fe14B at T = 0 (K).

determined by the competition of the coefficients \( A_l^0 \{ r^l \} \Theta_l \) up to the 6-th order. With increasing temperature, the minimum of the total MA energy in H0.5Fe14B is shifted to \( \theta = 0^\circ \) shown in Fig. 3(d), as expected from the temperature dependence of the tilt angle shown in Fig. 2. We have also confirmed that in both systems, the contribution of higher order term \( A_l^m \) \((l \geq 4)\) to the local MA decreases with increasing temperature as with the study by Kuz’min.29

The magnetic structure of the entire system is determined by the minimum of the free energy of the whole system. The direction of \( m \) and \( \theta_{Fe} \) and those of the Ho magnetic moment \( \Delta \theta_{gi} \) on the \( f_i \) \((g_i) \) sites at \( T = 0 \) \( (K) \) are shown in Fig. 4. The R magnetic moments are essentially antiparallel to the Fe magnetic moment; however, a small noncollinear magnetic structure appears owing to the inequivalent value of the local MA. The relatively large deviation of the magnetic moment on the \( f_2 \) site is related to the local MA energy having a minimum at \( \theta \geq \theta_{Fe} \) in Fig. 3(c); however, the deviation from \( \theta_{Fe} \) is mere 4°. This means that the R moments are forced to align by the strong \( H_m \). These results may be confirmed in a neutron scattering experiment. For Dy\(_2\)Fe\(_{14}\)B, \( \theta_{Fe} = 0^\circ \), and \( \Delta \theta_f = \Delta \theta_g = 0 \).

We calculated the site-specific CEF values of Ho\(_2\)Fe\(_{14}\)B and Dy\(_2\)Fe\(_{14}\)B using the first-principles method and constructed a spin model taking into account the calculated CEF and exchange field from the Fe magnetic moments. Our mean field results satisfactorily explained the SRT in Ho\(_2\)Fe\(_{14}\)B and the absence of the SRT in Dy\(_2\)Fe\(_{14}\)B. The inequivalence of the R site appears in the noncollinear magnetic structures in H0.5Fe\(_{14}\)B. This type of inequivalence of the R moments may also exist in R\(_2\)Fe\(_{14}\)B with light R ions. Haskel et al. performed XMCD measurements and reported site-dependent resonant magnetic scattering loops in Nd\(_2\)Fe\(_{14}\)B.13 They concluded that g-site Nd ions contribute more to the MA of Nd\(_3\)Fe\(_{14}\)B than f-site ions. In contrast to their conclusion, the present results in Fig. 3 indicate that the inequivalence of the R site is not so important to the total MA in the thermal equilibrium state.

In conclusion, an effective spin model based on the CEF values calculated by the first-principles method adequately reproduces the SRT in H0.5Fe\(_{14}\)B and Dy\(_2\)Fe\(_{14}\)B. The phenomenon is explained well in terms of the MA of R ions including up to the 6-th order CEF parameters. The

\[ \theta_{Fe} = 19^\circ \]

\[ \Delta \theta_f = 23^\circ \]

\[ \Delta \theta_g = 19^\circ \]

\[ \Delta \theta_f = 16^\circ \]

\[ \Delta \theta_g = 18^\circ \]

\[ \theta_{Fe} = 0^\circ \]

\[ \Delta \theta_f = \Delta \theta_g = 0 \]

in inequivalence of \( R \) ions affects the noncollinear magnetic structure of these permanent magnets. A further theoretical study of R\(_2\)Fe\(_{14}\)B with light \( R \) elements is desirable.

The authors thank Professor P. Novák and J. Inoue for helpful discussion and critical reading of this manuscript. This work was supported by the Elements Strategy Initiative Center for Magnetic Materials (ESICM) under the auspices of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). Some of the numerical computations in this work were performed at the Yukawa Institute Computer Facility and also at the Cyberscience Center, Tohoku University.