Theoretical evaluation of the temperature dependence of magnetic anisotropy constants of Nd$_2$Fe$_{14}$B: Effects of exchange field and crystal field strength

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Received January 9, 2015; accepted March 6, 2015; published online March 23, 2015

To identify the possible mechanism of the coercivity ($H_c$) degradation of Nd–Fe–B sintered magnets, we study the roles of the exchange field acting on the 4f electrons in Nd ions and theoretically investigate how variation in the exchange field affects the values of the magnetic anisotropy constants $K_1$ and $K_6$. We find that, with decreasing exchange field strength, both values decrease as a result of the lower asphericity of the 4f electron cloud, indicating that the local anisotropy constants might become small around the grain boundaries, where the exchange fields are reduced owing to the smaller coordination number. © 2015 The Japan Society of Applied Physics

Nd–Fe–B sintered magnets$^{1–3}$ have the largest maximum energy product among current magnets and have been widely used for magnetic devices such as voice coil motors in magnetic recording systems. Recently, because of the rapidly growing interest in electric vehicles, much effort has been made to suppress the degradation of the coercivity ($H_c$) of Nd–Fe–B magnets. However, from an industrial viewpoint, a reduction in the use of Dy is strongly desired, because Dy is a rare metal, and the magnetization of Nd–Fe–B magnets is decreased by substituting Dy for Nd owing to antiparallel coupling between the Dy and Fe moments. Realizing Dy-free high-performance Nd–Fe–B magnets requires a further increase in $H_c$ in the Nd–Fe–B system by microstructure optimization$^4$–$^11$ therefore, establishing the microscopic foundation of the coercivity mechanism is desired. From a theoretical viewpoint, many works$^{12–16}$ have focused on the change in the magnetic anisotropy constants around the grain boundary surfaces as a result of stresses, defects, and changes in the spatial symmetry. In addition, micromagnetic model calculations have shown that the surface c-plane anisotropy can dramatically decrease the coercivity.$^{17}$ For these reasons, evaluation of the local anisotropy constants around grain boundaries and determining their temperature dependence are important for investigating the degradation of the coercivity.

Regarding the magnetic anisotropy of rare earth (RE) transition metal compounds, it is believed that the 4f electrons in RE ions are responsible for the main part of the magnetic anisotropy and that the crystalline electric field (CEF) acting on the 4f electrons dominates this property.$^{18}$ Assuming that the exchange field on the 4f electrons is sufficiently strong, by using the CEF parameter $A_{0}^{0}$, the leading anisotropy constant $K_1$ can be approximately described by $K_1 = -3J(1-1/\alpha)(\vec{r}^2)A_{0}^{0}N_{R}$, where $\alpha$ is the Stevens factor, $J$ is the total angular momentum, $\langle \vec{r}^2 \rangle$ is the average of $\vec{r}^2$ over the radial wave function of the 4f electrons, and $N_{R}$ is the density of RE ions. Note that the CEF parameter is easily affected by the environment, especially around grain boundaries. Actually, Moriya et al.$^{15}$ predicted, using a first-principles calculation, that the CEF parameter $A_{0}^{0}$ is negative at the (001) surface of Nd$_2$Fe$_{14}$B. According to Ref. 17, this may dramatically degrade $H_c$.

Note that the exchange field acting on the 4f electrons from the surrounding Fe spins can also be changed as a result of the environment surrounding the RE ions. It is natural to consider that the exchange fields are weaker around the grain boundaries than in the bulk. In this case, the above expression for $K_1$ no longer applies because the precondition that the exchange field is sufficiently strong no longer holds. In particular, the decrease in the exchange field may significantly affect the temperature dependence of the anisotropy constants because of thermal fluctuations of the 4f moments. On the basis of this viewpoint, we focus on the effects of the exchange field on the 4f-related anisotropy constants, and we theoretically investigate how the magnetic anisotropy is affected by variations in the exchange fields and CEF acting on the 4f electrons, especially above room temperature. To this end, the temperature-dependent anisotropy constants $K_1(T)$ and $K_6(T)$ are calculated using crystal field theory.

Regarding the temperature dependence, several works in Ref. 3 and Skomski and Coey$^{19}$ have attempted to explain the temperature dependence of the magnetic anisotropy of Nd–Fe–B magnets. However, few studies have calculated the $K_1(T)$ curve itself from the microscopic viewpoint. Thus, one of our objectives is to realize theoretically the $K_1(T)$ and $K_6(T)$ curves for comparison with the experimental data. The other objective is to clarify quantitatively how the exchange field affects $K_1(T)$ and $K_6(T)$, especially above room temperature.

The calculation method we use here is based on conventional crystal field theory for the 4f electronic system in RE ions. The total Hamiltonian for 4f electrons is given as $\hat{H} = \hat{H}_{\text{ion}} + \hat{H}_{\text{CEF}} + \hat{H}_{\text{mag}}$, where $\hat{H}_{\text{ion}}$ describes the intraatomic interactions in an RE ion, $\hat{H}_{\text{CEF}}$ denotes the CEF part representing the electrostatic field acting on the 4f electrons from the surrounding charge, and $\hat{H}_{\text{mag}}$ denotes the effective exchange interactions between the 4f and Fe moments. When Nd ions are involved, only the ground $J$ multiplet can be considered as the 4f states because the 4f electrons of the Nd ion have large spin–orbit coupling compared to the CEF splitting. In this case, $\hat{H}_{\text{CEF}}$ can be written as $\hat{H}_{\text{CEF}} = \sum_{l=2}^{6}B_l^0 \hat{O}_l^0$, where $B_l^0 = \theta_l(r^l)A_l^0$ is the CEF coefficient, and $\hat{O}_l$ is the Stevens operator expressed by the multinomial of the orbital angular momentum operators. $\theta_l$ is the Stevens factor $\alpha$, $\beta$, or $\gamma$ for $l = 2$, 4, or 6, respectively, and $A_l^0$ are the CEF parameters. In this work, we take into account only $B_2^0$, $B_4^0$, and $B_6^0$, for simplicity. Actually, as shown by Yamada et al.$^{18}$ the terms $B_2^0$ are canceled out when one sums up the terms on the four nonequivalent RE sites in a unit cell of Nd$_2$Fe$_{14}$B, because of the relation $B_l^0(1) = -B_l^0(2), B_l^0(3) = -B_l^0(4)$, where the numbers in parentheses indicate the nonequivalent site in a unit cell. Although this is true only when the amplitude of the exchange field is sufficiently large relative to the CEF, we confirmed that these...
terms make small contributions to $K_1$ and $K_2$ when we take the average over the RE sites. Furthermore, we also confirmed that the $K_3$ term representing four-fold in-plane anisotropy rapidly decreases above room temperature. Within the ground $J$ multiplet, $\hat{H}_{\text{mag}}$ can be expressed as $\hat{H}_{\text{mag}} = 2(g_J - 1)\mathbf{J} \cdot \mathbf{H}_{\text{ex}}$, where $g_J$ is the Landé factor, and $\mathbf{H}_{\text{ex}}$ is the effective exchange field reflecting the exchange interaction with the surrounding Fe spins. In principle, $\mathbf{H}_{\text{ex}}$ depends on the temperature through a self-consistent equation for a molecular field approximation in the full system of Nd$_2$Fe$_{14}$B. However, in this work, we assume that $\mathbf{H}_{\text{ex}}$ is proportional to a molecular field of Fe spins ($\langle S_{\text{Fe}} \rangle$) and that the molecular field is described by the Heisenberg model for the Fe spin system. Solving the self-consistent equation for $\langle S_{\text{Fe}} \rangle$ under the condition that the spin of the Fe ion is 1 and that the Curie temperature $T_c$ is 583 K, we have confirmed that $\langle S_{\text{Fe}} \rangle$ reproduces well the temperature dependence of the magnetization of Y$_2$Fe$_{14}$B.\textsuperscript{19} Thus, we have introduced the temperature dependence in $\mathbf{H}_{\text{ex}}$ as $\mathbf{H}_{\text{ex}}(T) = \mathbf{H}_{\text{ex}}(\langle S_{\text{Fe}} \rangle)$, where $\mathbf{H}_{\text{ex}}$ is the strength parameter of the effective exchange field. Here, the direction of the total magnetization is assumed to coincide with that of $\mathbf{H}_{\text{ex}}$, because the total magnetization is governed mostly by the Fe moments even when the direction of the 4f moments differs from that of the Fe moments.

By defining $\theta$ as the angle between $\mathbf{H}_{\text{ex}}(T)$ (the total magnetization) and the $c$-axis of the crystal lattice, the free energy of the 4f electronic system can be written as

$$F(\theta, T) = -k_B T \ln \text{Tr} \exp \left[ -\frac{\hat{H}(\theta, T)}{k_B T} \right],$$

where the eigenvalues are calculated by diagonalizing $\hat{H}(\theta, T)$ within the $J = 9/2$ subspace (10 × 10 matrix), and $F(\theta, T)$ is numerically obtained.

The 4f-related anisotropy constants $K_1$ and $K_2$ are coefficients of $\sin^2 \theta$ and $\sin \theta$ in $F(\theta, T)$. For small $\theta$, $F(\theta, T)$ can be expanded as

$$F(\theta, T) = F(0, T) + \frac{\theta^2}{2} F^{(2)}(0, T) + \frac{\theta^4}{4!} F^{(4)}(0, T) + \cdots$$

$$\equiv F(0, T) + K_1(T) \theta^2$$

$$+ \left[ -\frac{2}{3} K_1(T) + K_2(T) \right] \theta^4 + \cdots.$$  

Therefore, $K_1$ and $K_2$ can be expressed by

$$K_1(T) = \frac{1}{2} F^{(2)}(0, T),$$

$$K_2(T) = \frac{1}{3} K_1(T) + \frac{1}{4!} F^{(4)}(0, T),$$

where to calculate $F^{(2)}(0, T)$ and $F^{(4)}(0, T)$ from the finite differences.

To analyze the magnetic anisotropy constants of Nd$_2$Fe$_{14}$B quantitatively, we start by reproducing the experimentally obtained $K_1$ and $K_2$ values of bulk Nd$_2$Fe$_{14}$B using the present approach. Figure 1 shows the calculated results obtained for $K_1(T)$ and $K_2(T)$ using $A_{\text{eff}}' = 450 \text{ K}/\mu_B^2$, $A_{\text{eff}}'' = -45 \text{ K}/\mu_B^2$, $A_{\text{eff}}''' = -0.1 \text{ K}/\mu_B^6$, and $\mathbf{H}_{\text{ex}} = 364 \text{ K}$.\textsuperscript{21} Here, $\mu_B$ is the Bohr magneton. In calculating $K_1(T)$, we add the Fe sublattice contribution $K_{\text{Fe}}^{\text{mag}}(T)$ deduced from experimental data for Y$_2$Fe$_{14}$B.\textsuperscript{20} This has an almost constant value of $\sim 1 \text{ MJ/m}^3$ below 300 K and decreases to zero when the temperature approaches $T_c$. The difference between two Nd sublattices is not taken into account here. The inset in Fig. 1 shows the tilting angle of the magnetization vector calculated from $\partial F(\theta, T)/\partial \theta = 0$. When this spin reorientation behavior is included, the calculated and experimental data agree to a certain degree.

Note that the experimental values of $K_1(T)$ and $K_2(T)$ are not obtained by direct measurement but are usually deduced from magnetization curves or torque curves under finite applied fields. Furthermore, in our numerical analysis, we made some approximations to express $K_1(T)$ and $K_2(T)$. In this sense, we believe that the CEF and $\mathbf{H}_{\text{ex}}$ parameters reported by Yamada et al.\textsuperscript{18} are more reliable, because in their analysis the Zeeman term is considered in addition to the Hamiltonian to ascertain the magnetization curves and to compare them directly with the measured ones. Reflecting this difference, the CEF and $\mathbf{H}_{\text{ex}}$ parameters obtained by Yamada et al. differ considerably from ours. To examine the availability of the present method and reliability of the parameters obtained above, we also calculated the $K_1(T)$ and $K_2(T)$ curves using the parameters given by Yamada et al.\textsuperscript{18} Except for the behavior of $K_2(T)$ below 70 K, we confirmed that the calculated data agree with both the experimental data and our calculated results. These results lead us to believe that the present analysis and the parameters obtained here can provide an appropriate quantitative characterization of $K_1(T)$ and $K_2(T)$ at least above 100 K. Further, we emphasize that this discrepancy does not critically influence our main conclusion.

Next we proceed to examine how $K_1(T)$ and $K_2(T)$ are affected by variation in the amplitude of $\mathbf{H}_{\text{ex}}(T)$. Figure 2 shows the calculated $K_1(T)$ and $K_2(T)$ using the half-value of $\mathbf{H}_{\text{ex}}$ with the other parameters unchanged. The results in Fig. 1 are also shown for comparison. A steep reduction in both $K_1(T)$ and $K_2(T)$ appears near 70 K. Consequently, for temperatures above 200 K, the values of both $K_1$ and $K_2$ become smaller than those in Fig. 1. To see the $\mathbf{H}_{\text{ex}}$ dependence of the values of $K_1$ and $K_2$, in Fig. 3, we plot these...
values as a function of $H_{\text{ex}}$ at $T = 300\,\text{K}$. In these calculations, we neglect the Fe contribution $K_{\text{ex}}^{\text{Fe}}(T)$ and focus only on the effects of $H_{\text{ex}}$ on the 4f-related anisotropy constants. $K_2$ increases monotonically with $H_{\text{ex}}$, whereas $K_1$ has a peak at around $H_{\text{ex}} = 300\,\text{K}$ and becomes negative above $H_{\text{ex}} = 800\,\text{K}$. The negative value of $K_1$ in the high-$H_{\text{ex}}$ region is naturally understood by considering the fact that $K_1$ starts from a negative value at $T = 0$; that is, the high limit of $H_{\text{ex}}$ effectively corresponds to the low-temperature limit. Further attention should be paid to the low-$H_{\text{ex}}$ region below $H_{\text{ex}} = 300\,\text{K}$, where both $K_1$ and $K_2$ decrease with decreasing $H_{\text{ex}}$. This is because the 4f electron cloud approaches a spherical shape, in accordance with the decrease in $H_{\text{ex}}$, resulting in an insensitivity to the CEF and a decrease in the anisotropy energy. This behavior indicates that the temperature dependence of the anisotropy constants $K_1$ and $K_2$ comes not only from thermal fluctuation of the 4f moments but also from the strength of $H_{\text{ex}}(T)$ through its temperature dependence as $\langle S_{\text{Fe}} \rangle$. This can explain the vanishing of $K_1$, $K_2$, and hence $H_e$ at the Curie temperature. Further, even at a lower temperature, the anisotropy constants may become small around the grain boundaries, where the exchange fields become small owing to the smaller coordination number or to other factors such as stresses and lattice defects. For these reasons, at around the operating temperature of electric vehicle motors ($\sim 500\,\text{K}$), the decrease in the amplitude of $H_{\text{ex}}$, in addition to the reduction in $\langle S_{\text{Fe}} \rangle$ owing to its temperature dependence, may significantly influence magnet performance.

Finally, we investigate the effects of variation in the CEF parameters on $K_1(T)$ and $K_2(T)$. As pointed out in our previous work,\textsuperscript{15} it may be possible that $A_2^0$ is negative at the grain surfaces, depending on whether their characteristics differ from those of the bulk. Figure 4 shows the behaviors of $K_1(T)$ and $K_2(T)$ using the parameters $A_1^0 = -450\,\text{K}/a_0^2$, $A_2^0 = A_6^0 = 0$, and $H_{\text{ex}} = 364\,\text{K}$. Clearly, $K_1(T)$ is negative at any temperature, and $K_2(T)$ vanishes at temperatures above $200\,\text{K}$, which implies that the system favors planar anisotropy above $200\,\text{K}$. Thus, the prediction of $K < 0$ when $A_2^0 < 0$ reported in the previous study is justified in the room-temperature region, from which Mitsumata et al.\textsuperscript{17} suggested that $H_e$ is dramatically degraded owing to the negative $K$ at the surface.

In conclusion, we summarize our study as follows. To identify the possible mechanism of the coercivity ($H_e$) degradation of Nd–Fe–B sintered magnets, we investigated how the magnetic anisotropy is affected by variation in the exchange fields and CEF acting on the 4f electrons. To this end, the temperature-dependent anisotropy constants $K_1(T)$ and $K_2(T)$ were calculated using crystal field theory. Using a certain set of CEF parameters and exchange field strength, we can obtain $K_1(T)$ and $K_2(T)$ curves that reproduce well the experimental data for bulk Nd$_2$Fe$_{14}$B. Both values were found to decrease with decreasing exchange field strength as a result of the lower asphericity of the 4f electron cloud. This feature makes $K_1(T)$, $K_2(T)$, and hence $H_e$ vanish at the Curie temperature, where the exchange field strength tends to zero. Even at a lower temperature, the anisotropy constants may become small around the grain boundaries, where the exchange fields become small owing to the smaller coordination number or to other factors such as stresses and lattice defects. For these reasons, at around the operating temperature of electric vehicle motors ($\sim 500\,\text{K}$), the decrease in the amplitude of $H_{\text{ex}}$, in addition to the reduction in $\langle S_{\text{Fe}} \rangle$ owing to its temperature dependence, may significantly influence magnet performance. We also confirmed that the negative value of $A_2^0$, the leading CEF parameter, results in planar anisotropy at room temperature. Thus, the prediction of $K < 0$ when $A_2^0 < 0$ reported in the previous study is justified in the room-temperature region.

**Acknowledgment** This work was supported by JST-CREST.
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