Understanding and controlling magnetic anisotropy is a central issue in developing magnetic devices such as spin random-access memories (RAMs), high-density storage, and permanent magnets. Magnetic anisotropy at room temperature or above is important at a practical level and should be evaluated by considering the temperature dependence on materials whose magnetic properties strongly depend on temperature. This article presents appropriate expressions for computing temperature-dependent magnetic anisotropy constants (MACs) and their physical interpretation.

Early studies on the temperature dependence of magnetocrystalline anisotropy were first performed by Zener,\textsuperscript{1,3} followed by Callen and Callen.\textsuperscript{2,3} By considering an insulated ferromagnet having localized moments, they phenomenologically derived a very simple expression called the Callen–Callen law: $K_n(T)/K_n(0) = M(T)/M(0)$, where $K_n(T)$ is the $n$th-order MAC at the temperature $T$ and $M$ is the magnetization. This theory is based on the concept that a decrease in the MAC originates from the breakdown in the asphericity of the electron cloud of the magnetic ions due to thermal excitation.\textsuperscript{24} Because a spherical electron cloud means the absence of a specific direction for the magnetic polarization (note that this does not mean the disappearance of the local moment), the temperature dependence of the MAC can be related to that of the magnetization, as shown above. After this pioneering work, there have been few theoretical works on the temperature dependence of MACs. Much later, Skomski et al.\textsuperscript{5,7} discussed the Callen–Callen law by analyzing various magnetic materials and showed that it can be applied to simple systems such as Fe and Co. However, they also pointed out that complex magnetic materials such as NdCo$_5$ and Nd$_2$Fe$_{14}$B do not obey this law; instead, they exhibit a spin reorientation. Thus, the Callen–Callen law does not always provide a quantitatively satisfactory range of applicability.

In recent years, theoretical trials have been conducted to evaluate the magnetocrystalline anisotropy energy (MAE) of spin Hamiltonians at a finite temperature, including the magnetic anisotropy term, with a Monte Carlo approach.\textsuperscript{8,9} From a technological viewpoint, micromagnetic simulations of the Landau–Lifshitz–Gilbert equation, including a random field describing thermal noise,\textsuperscript{5,10–12} and the Landau–Lifshitz–Bloch equation\textsuperscript{13,14} have been performed to observe the thermal stabilization of the magnetization.

The MACs at $T = 0$ of transition-metal systems and rare-earth (RE) compounds have been calculated by using a first-principles approach, and the results have provided satisfactory numerical accuracy compared with the experimental data. For transition-metal systems, considerable effort has been made to clarify the effects of practical factors such as the interfaces\textsuperscript{15,16} and distortion\textsuperscript{17} in magnetic multilayers and the chemical disorder\textsuperscript{18,19} in alloys on the MAE. For the finite-temperature treatment within the first-principles approach, Staunton et al.\textsuperscript{20} and Matsumoto et al.\textsuperscript{21} successfully demonstrated the temperature dependence of the MAEs of FePt and YCo$_5$, respectively, on the basis of the functional integral method. For RE compounds, the MACs at $T = 0$ have been successfully evaluated by calculation of the crystalline electric field (CEF) acting on the 4f electrons in the RE ions based on the first-principles approach.\textsuperscript{22–24} All of the approaches mentioned above have seen rapid developments in the past two decades owing to the considerable progress in numerical techniques and computer performance.

Recently, we theoretically studied the temperature dependence of $K_1$ and $K_2$ of Nd$_2$Fe$_{14}$B and reproduced the experimental data for $K_1(T)$ well by using appropriate crystalline field parameters.\textsuperscript{25} In that work, we evaluated $K_1(T)$ by numerical differentiation of the free energy with respect to the magnetization direction and investigated the effects of the exchange field and CEF on the magnetic anisotropy of Nd$_2$Fe$_{14}$B. However, it is still difficult to measure $K_1$ directly, especially at a finite temperature, because of the lack of an explicit quantitative expression for $K_1$. Given this background, our purpose in the present work was to develop a standard framework to directly discuss magnetic anisotropy.

In this article, we provide a general expression for $K_n$, starting from the Hamiltonian describing the magnetic system, and present a method to evaluate $K_n$ quantitatively for realistic ferromagnetic systems. In particular, we demonstrate that the proposed method is useful and convenient for evaluating the temperature dependence of $K_n(T)$ for localized electronic systems such as RE compounds or systems that can be described only by angular momentum operators.

First, we derive the microscopic expression for the first-order MAC $K_1(T)$ of crystals with $N$-fold rotational symmetry ($N \geq 3$). By introducing the Helmholtz free energy $F(\theta, \phi) := -\beta^{-1} \ln \sum_{\mu} \exp[-\beta E_{\mu}(\theta, \phi)]$ and comparing $F(\theta, \phi)$ with the phenomenological expression,\textsuperscript{26,27} we have the relation

$$K_1(T) = \frac{1}{2} \frac{\partial^2 F(\theta, \phi)}{\partial \theta^2} |_{\theta = 0},$$

where $\beta := 1/(k_B T)$ is the inverse temperature corresponding to $T$ and $E_{\mu}(\theta, \phi)$ is an energy eigenvalue of the Hamiltonian $H(\theta, \phi)$. The parameters $\theta$ and $\phi$ are the zenithal and azimuthal angles, respectively, that denote the direction of the magnetization relative to the $c$-axis. Here, we consider...
cases where the Hamiltonian is explicitly written as a linear function with respect to the magnetization direction:

\[
\mathcal{H}(\theta, \phi) \equiv \hat{h} + m(\theta, \phi) \cdot \hat{D},
\]

where \(m(\theta, \phi) \equiv (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)\) and \(\hat{h}\) is the angle-independent part (the hat denotes an operator). \(\hat{D}\) is an operator with the transformation property

\[
\hat{C}_N \hat{D}^z \hat{C}_N = e^{i\frac{\pi}{2} N} \hat{D}^z,
\]

\[
\hat{C}_N \hat{D}^z \hat{C}_N = \hat{D}^z,
\]

where \(\hat{D}^z \equiv \hat{D}^z \pm i \hat{D}^x\), and \(\hat{C}_N\) is the N-fold rotation symmetry operator around the symmetrical axis parallel to the e-axis. Based on the derivatives of \(E_n(\theta, \phi)\), the derivatives of \(F(\theta, \phi)\) are expressed as follows:

\[
\partial_\theta F = \sum_n e^{-\beta E_n} \partial_\theta E_n,
\]

\[
\partial_\theta F = \sum_n e^{-\beta E_n} \partial_\theta E_n - \beta [\partial_\theta E_n]^2 + \beta (\partial_\theta F)^2.
\]

Under the purely theoretical treatment, the MACs can be described in terms of \(E_n(\theta, \phi)\) in the vicinity of \(\theta = 0\). By introducing \(\mathcal{H}(\theta, \phi) \equiv m(\theta, \phi) \cdot \hat{D} - \hat{D}^z\), we can divide the Hamiltonian \(\mathcal{H}(\theta, \phi)\) into the non-perturbative part \(\mathcal{H}_{\theta=0} \equiv \hat{h} + \hat{D}^z\) and perturbative part \(\mathcal{V}(\theta, \phi)\). Here, note \(\mathcal{V}(\theta, \phi) \rightarrow 0\) in the limit \(\theta \rightarrow 0\) and

\[
[\hat{C}_N, \mathcal{H}_{\theta=0}] = 0.
\]

To obtain \(K_1\), we can perturbatively calculate \(E_n\) up to the second order in \(\mathcal{V}\). We assume that the unperturbed eigenvalues \(\epsilon_n\) and eigenstates \(|n\rangle\) are given. This satisfies

\[
K_1(T) = -\frac{1}{8} \langle \{\hat{J}^+, \{\hat{J}^+, \hat{h}\}\} \rangle + \frac{1}{4} \sum_n e^{-\beta (\epsilon_n - F_0)} \sum_{k \neq n} \frac{|\langle n| \hat{J}^+, \hat{h} |k\rangle|^2 + |\langle k| \hat{J}^+, \hat{h} |n\rangle|^2}{\epsilon_n - \epsilon_k},
\]

where \(\langle \cdot, \cdot \rangle\) denotes the statistical average in \(\mathcal{H}_{\theta=0}\). This is another of the main results that is appropriate for describing physical pictures of the magnetic anisotropy because the commutators distill the essential features from the Hamiltonian. Equations (8) and (11) are equivalent and general for \(K_1\).

For example, let us apply these formulas to localized spin systems. Consider the single-spin Hamiltonian

\[
\mathcal{H}_{\text{spin}} := -A \hat{S}^2 - 2H_{\text{ex}} \cdot \hat{S},
\]

where \(\hat{S}\) is a spin operator, \(A\) is the single-ion MAE, \(H_{\text{ex}}\) is the exchange field parallel to the magnetization direction (i.e., \(H_{\text{ex}} \equiv H_{\text{ex}}(m)\)), and the condition \(A < 2H_{\text{ex}}\) is assumed. Hence, we find the correspondences \(\hat{D} \rightarrow -2H_{\text{ex}} \hat{S}\) and \(\hat{h} \rightarrow -A \hat{S}^2\). Obviously, \(\hat{S}\) satisfies the conditions in Eqs. (9) and (10) as \(\hat{J}\). Then, the commutators are calculated as \([\hat{S}^+, -A \hat{S}^2] = A(\hat{S}^+ \hat{S}^2 + \hat{S}^2 \hat{S}^+)\) and \([\hat{S}^-, -A \hat{S}^2] = 2A(\hat{S}^2 - 3(\hat{S}^2)^2)\). From Eq. (11),

\[
K_1^{\text{spin}}(T) = -\frac{A}{2} \left[ S(S + 1) - 3 \sum_{M=-S}^{S} e^{-\beta (\epsilon_n - F_0)} M^2 \right]
+ \frac{1}{4} \sum_{M=-S}^{S} e^{-\beta (\epsilon_n - F_0)} \left[ \frac{A^2(1 - 2M)^2(S + M)(S + M + 1)}{A(1 - 2M) - 2H_{\text{ex}}} \right]
+ \frac{A^2(1 + 2M)^2(S - M)(S + M + 1)}{A(1 + 2M) + 2H_{\text{ex}}},
\]

where \(\epsilon_n^{\text{spin}} := -AM^2 - 2H_{\text{ex}} M\) is an energy eigenvalue of \(\mathcal{H}_{\text{spin}}^{\text{spin}} \equiv -A \hat{S}^2 - 2H_{\text{ex}} \hat{S}\) and \(F_0^{\text{spin}} := -\beta^{-1} \ln \sum_{M=-S}^{S} \exp(-\beta \epsilon_n^{\text{spin}})\). In the special cases where \(A \rightarrow 0\) and/or \(H_{\text{ex}} \rightarrow 0\), we obtain \(K_1^{\text{spin}}(T) \rightarrow 0\). This confirms that \(K_1^{\text{spin}}(T)\) vanishes above the Curie temperature where \(H_{\text{ex}} = 0\). At \(T = 0\) and as \(T \rightarrow \infty\), we also have

\[
K_1^{\text{spin}}(0) = \left( \frac{1}{AS[1 - (2S)^{-1}]} + \frac{1}{H_{\text{ex}} S} \right)^{-1},
\]

\[
K_1^{\text{spin}}(\infty) = 0.
\]
The zero-temperature value is exactly obtained as
\[ a(0) = \frac{3 + A(S - 3/2)/\Delta H_{ex}}{1 + A(S - 3/2)/\Delta H_{ex}}. \]  
(17)

For the classical limit under the condition of fixed \( AS^2 \) and \( \Delta H_{ex} S \),
\[ a(0) \to \frac{3 + AS^2/(\Delta H_{ex} S)}{1 + AS^2/\Delta H_{ex} S}. \]  
(18)

In either case, our formula shows that \( a(0) \approx 1 \) under the condition \( AS^2/(\Delta H_{ex} S) \gg 1 \) and \( a(0) \approx 3 \) for \( AS^2/\Delta H_{ex} S \ll 1 \). In particular, our formula supports the Callen–Callen law: \( a(0) = 3 \) under the latter condition. This result is reasonable because the Callen and Callen theory is based on the perturbative theory with respect to the anisotropy energy. Figure 1 shows the temperature dependence of various quantities at \( S = 1 \) and \( \Delta H_{ex} = 0.1 \). We can observe that \( a(0) \) slightly deviates from the Callen–Callen law because of corrections from the higher-order terms with respect to \( AS/\Delta H_{ex} \).

The other example is a localized 4f-electron system. Here, we consider a model in which 4f electrons are in ligand and exchange fields.\(^{26-29}\)

\[ K_1'(T) = -\frac{\lambda}{4} \langle \mathbf{L}_n \cdot \mathbf{S}_i + \mathbf{L}_i \cdot \mathbf{S}_n \rangle + \frac{\lambda^2}{2} \sum_{k,j} \exp(-\beta \varepsilon_k - F_j) \sum_{k,l} |\langle \mathbf{L}_i \cdot \mathbf{S}_n | k\rangle|^2 \frac{(n \leftrightarrow k)}{\varepsilon_n - \varepsilon_k}. \]  
(20)

At first glance, we can understand that \( K_1' \) vanishes in the absence of the spin–orbit interaction. Now, we can perturbatively evaluate Eq. (20) with respect to \( \lambda \) to the second order under the assumption that the CEF has tetragonal symmetry. The straightforward calculation gives

\[ K_1'(T) \approx \lambda^2 \sum_{k,j} \frac{4\Delta L_{nk} - \Delta L_{nk}^+ - \Delta L_{nk}^-}{\varepsilon_k - \varepsilon_n}. \]  
(21)

where \( \Delta L_{nk} := \langle \mathbf{L}_i \cdot \mathbf{S}_n | k\rangle^2 - \langle \mathbf{L}_i \cdot \mathbf{S}_n | n\rangle^2 \). This is a localized spin system version of the first-order MAC in itinerant electronic systems.\(^{30-33}\) Here, note that we can also regard \( \mathbf{J}_f := \mathbf{L} + \mathbf{S}_f \) as \( \mathbf{J}_f \) where \( \mathbf{L} + \mathbf{S}_f = 0 \). This choice leads to another form:

\[ K_1'(T) = -\frac{1}{2} \langle [\mathbf{L}_i, [\mathbf{L}_i, \mathbf{H}_{\text{cry}}]] \rangle + \text{h.c.} + \frac{1}{2} \sum_{k,j} \exp(-\beta \varepsilon_k - F_j) \sum_{k,l} |\langle \mathbf{L}_i \cdot \mathbf{S}_n | k\rangle|^2 \frac{(n \leftrightarrow k)}{\varepsilon_n - \varepsilon_k}. \]  
(22)

where we use \( [\mathbf{J}_f, \mathbf{L} \cdot \mathbf{S}_f] = 0 \) and \( [\mathbf{S}_f, \mathbf{H}_{\text{cry}}] = 0 \). Thus, we can easily confirm that \( K_1'(T) = 0 \) when \( \mathbf{H}_{\text{cry}} = 0 \). The commutators can be calculated by representing \( \mathbf{H}_{\text{cry}} \) in terms of spherical tensor operators constructed from \( \mathbf{L}_i \) on the basis of the Wigner–Eckart theorem. For simplicity, let us consider the minimum case that

\[ \mathbf{H}_{\text{cry}} = C_{\lambda}^2 \mathbf{L}_i^2 \]  
(23)

for \( \lambda \to \infty \), where \( C_{\lambda}^2 = \text{constant encoding a CEF} \). The commutators can be calculated as \( [\mathbf{L}_i, [\mathbf{L}_i, \mathbf{H}_{\text{cry}}]] = -C_{\lambda}^2 [2\mathbf{L}_i - 6\mathbf{L}_i^2] \), and the second term in Eq. (22) vanishes at the limit of a large exchange field such that \( K_1'(T) = \frac{\lambda^2}{4} C_{\lambda}^2 [2\mathbf{L}_i - 3\mathbf{L}_i^2] \). Then, by replacing \( \mathbf{L}_i \) by \( \mathbf{J}_f \) on the basis of the equivalent-operator technique\(^{34,35}\) for \( \lambda \to \infty \), we have \( K_1'(T) = \frac{3}{2} B_{\lambda}^2 (\mathbf{J}_f - 3\mathbf{J}_f^2) \). Therefore, for light RE elements, our formula reproduces

\[ K_1'(T) = -3J(1/2)B_{\lambda}^2, \]  
(24)

where \( B_{\lambda}^2 \) is a CEF parameter and \( J \) is the total angular momentum.\(^{26}\) Note that, in the limit of \( \Delta H_{ex} \to 0 \), we observe \( K_1' \to 0 \) because the first and second terms in Eq. (22) are canceled.

Finally, we present numerical calculations for the temperature-dependent MACs (\( K_1, K_2, \) and \( K_3 \)) of Nd2Fe14B. The magnetic properties of the R2Fe14B systems (R is a rare earth element) can be well-described by the Hamiltonian in Eq. (19). The CEF is represented by \( \mathbf{H}_{\text{cry}} = \sum_{\varphi} \theta_{\varphi} \langle \mathbf{r} \rangle \hat{\mathbf{A}}_{\varphi}^2 \mathbf{O}_{\varphi}^{\text{CEF}} \) in terms of the Stevens operator \( \mathbf{O}_{\varphi} \), where \( \theta_{\varphi} \) is the Stevens factor determined geometrically. \( \langle \mathbf{r} \rangle \) is the expectation value of \( \mathbf{r} \) over the wave function of the 4f electrons, and \( \hat{\mathbf{A}}_{\varphi} \) is the parameter characterizing the CEF. The second-order and third-order MACs are represented by \( K_2 = K_1/3 + \frac{d_2}{\theta_{\varphi} \langle \mathbf{r} \rangle} \) and \( K_3 = \frac{d_3}{\theta_{\varphi} \langle \mathbf{r} \rangle} \), respectively. To evaluate the fourth-order derivative of \( \mathbf{F}(\theta, \phi) \), we have to calculate \( E_{\varphi} \) perturbatively up to the fourth order. Following the derivation of Eq. (8), the microscopic expressions of \( K_2 \) and \( K_3 \) are obtained as

\[ \frac{d_2}{\theta_{\varphi} \langle \mathbf{r} \rangle} = \sigma_\alpha. \]

\[ \frac{d_3}{\theta_{\varphi} \langle \mathbf{r} \rangle} = \sigma_\alpha. \]

\[ \frac{d_4}{\theta_{\varphi} \langle \mathbf{r} \rangle} = \sigma_\alpha. \]
We can ignore the temperature dependence of the exchange interaction of significant magnitudes is avoided. See Refs. 26 and 28 for detailed computational methods for solving the eigenproblems. Figure 2 shows the temperature dependence of the MACs for NdFe$_{13}$B calculated by using Eqs. (8), (25), and (26). As demonstrated in the dotted lines, we were able to reproduce $K_1$ and $K_2$ from our previous results, and we obtained $K_3(T) = 0$ because only $A_{2}^0$, $A_{2}^6$, and $A_{2}^8$ were used in that work. The solid lines denote the MACs calculated under the assumption that $A_{2}^0 = -30 K/a_0^6$ and the other parameters are the same as those for the dotted lines. The presence of a non-zero $A_{2}^0$ breaks the rotational symmetry around the $c$-axis; therefore, $K_3$ appears. Here, we do not repeat the discussion of the comparison with experimental results (see Ref. 25).

In summary, we derived direct expressions for the MACs at a finite temperature from a microscopic viewpoint. It is only assumed that the Hamiltonian is a linear function with respect to the magnetization direction. We discussed in detail the first-order constant $K_1$ and showed that the results reproduced previous results. Furthermore, we successfully calculated the temperature-dependent $K_1$, $K_2$, and $K_3$ for NdFe$_{13}$B.

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