Statistical and Analytical Approaches to Finite Temperature Magnetic Properties of SmFe$_{12}$ compound

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To investigate the magnetic properties of SmFe$_{12}$, we construct an effective spin model, where magnetic moments, crystal field (CF) parameters, and exchange fields at 0 K are determined by first principles. Finite temperature magnetic properties are investigated by using this model. We further develop an analytical method with strong mixing of states with different quantum number of angular momentum $J$ ($J$-mixing), which is caused by strong exchange field acting on spin component of 4f electrons. Comparing our analytical results with those calculated by Boltzmann statistics, we clarify that the previous analytical studies for Sm transition metal compounds over-estimate the $J$-mixing effects. The present method enables us to make quantitative analysis of temperature dependence of magnetic anisotropy (MA) with high-reliability. The analytical method with model approximations reveals that the $J$-mixing caused by exchange field increases spin angular momentum, which enhances the absolute value of orbital angular momentum and MA constants via spin-orbit interaction. It is also clarified that these $J$-mixing effects remain even above room temperature. Magnetization of SmFe$_{12}$ shows peculiar field dependence known as first-order magnetization process (FOMP), where the magnetization shows an abrupt change at certain magnetic field. The result of the analysis shows that the origin of FOMP is attributed to competitive MA constants between positive $K_1$ and negative $K_2$. The sign of $K_{1(2)}$ appears due to an increase in $d$ potential denoted by the parameter $A^d_{0}(r^2)$ ($A^d_{6}(r^4)$) caused by hybridization between 3d-electrons of Fe on 8i (8j) site and 5d and 6p valence electrons on Sm site. It is verified that the requirement for the appearance of FOMP is given as $-K_2 < K_1 < -6K_2$.

I. INTRODUCTION

There have been intensive studies on developing new rare-earth ($R$) lean permanent magnetic materials which have strong magnetic properties comparable to those of Nd-Fe-B. Nitrogenated compounds as NdFe$_{12}$N or NdFe$_{11}$TiN have been considered to be candidates of such materials, and thus series of experimental and theoretical efforts have been made to figure out the magnetic properties of these materials.$^{1-2}$. SmFe$_{12}$ with the ThMn$_{12}$ structure (Fig. 1) is also a possible candidate and has attracted renewed interest because it exhibits excellent intrinsic magnetic properties such as uniaxial magnetocrystalline anisotropy.$^{3,4}$ Although SmFe$_{12}$ itself is thermodynamically unstable, it has been known that the substitution of Fe with a stabilizing element, such as Ti or V, can remove this difficulty.$^{5-8}$. In these systems, however, the saturated magnetization is reduced due to anti-parallel alignment of magnetic moments of Ti and V relative to those of Fe. Recent development of the synthesis technology made it possible to fabricate highly textured single phase samples of SmFe$_{12}$ thin films.$^{9-12}$, and it has been shown experimentally that Co substitution for Fe enhances their magnetic properties, such as Curie temperature and magnetic anisotropy (MA).$^{13-15}$. Thus, SmFe$_{12}$-based systems belong to one of the most promising hard magnetic materials, and therefore to clarify the basic magnetic properties of SmFe$_{12}$ is crucially important.

![john.png](image)

FIG. 1. (color online) Crystal structure of SmFe$_{12}$ compound in ThMn$_{12}$ structure. Inequivalent sites: Sm(2a), Fe(8f), Fe(8i), and Fe(8j) are shown by different-colored balls and solid lines show interatomic short contacts less than 3.2 Å.

So far, many attempts have been performed for microscopic understanding of the magnetic properties of $R$ based permanent magnets.$^{16-20}$. Among them a powerful method is to combine the first-principle calculations for electronic states at the ground state with a suitable model for finite temperature properties.$^{21-23}$. As for SmFe$_{12}$, Harashima et al. (2015)$^{20}$, Körner et al (2016)$^{21}$ and Delonge et al (2017)$^{22}$ performed the first-principle calculations and model analysis of magnetic properties. In the theoretical study of Sm-based intermetallic compounds, however, there remains a basic issue how to deal with the formidably strong $J$-mixing effects in Sm. This
is the problem studied for a long period on the Sm-based magnets. There are some attempts to include the J-mixing in the analytical form by the first-order perturbation for the crystal fields (CFs). However, Kuz’min pointed out that the Sm-based magnetic materials are exceptional for application of the method.

We have recently developed a similar method, in which the model parameters are calculated by the first-principles and the finite temperature magnetic properties are calculated in a statistical way, and applied it to R₂Fe₁₄B systems. By taking into account CF parameters up to 6-th order, the model satisfactorily explained the experimental results for magnetization curves and the temperature dependence of MA constants. Using the method we recently calculated the temperature dependence of the MA constants of SmFe₁₂ and showed that K₁ > 0 and K₂ < 0 in consistence with experimental results. The report of the work, however, contains only the final results and no details of computational procedure have been presented. As a result no explanations on the mechanism for the results that K₁ > 0 and K₂ < 0 have been given.

The purpose of the present study is thus to clarify the origin of the finite temperature magnetic properties of SmFe₁₂ compound by statistical and analytical ways. To this end, we describe the details of the statistical method and develop a novel analytical method. The analytical procedure is able to derive simple relations between the temperature dependence of magnetic properties and parameters determined by first-principles electronic structure calculations. The treatment of the J-mixing effects adopted previously by the other groups will be modified, and the results will be compared with the statistical results of the temperature dependence of magnetic properties of SmFe₁₂. Good agreement between the analytical and statistical results guarantees the applicability of the modified analytical formula to Sm compounds.

In the following, we give the model Hamiltonian, the parameters of which are determined by the first-principles, and present the calculation procedure for finite temperatures, especially the statistical method to obtain the MA constants and magnetization curves, and explain the modified analytical method. The latter method may clarify the relations among the free energy of the system, the CF, and the exchange field. Using the analytical method, we will show that the mechanism of K₁ > 0 and K₂ < 0 in SmFe₁₂ is attributed to the characteristic lattice structure around Sm ions, that is, crystallographic 2b-sites on c-axis adjacent to Sm are vacant. We also present results on the magnetization process and nucleation fields by calculating Gibbs free energy. As pointed out in Ref., this analytical spin model can be easily extended to Sm ions around the intergranular phases, which is crucially important in the coercivity mechanism.

This paper is organized as follows. The model Hamiltonian is explained in Section II, and the procedure of the statistical and analytical method are explained in Section III. Section IV shows the results of temperature dependence of magnetic properties calculated in the statistical and analytical methods. A summary of our work is given in Section V.

II. MODEL HAMILTONIAN

We adopt a following Hamiltonian to investigate the magnetic properties of R transition metal (TM) compounds:

\[ \hat{H} = \frac{1}{V_0} \sum_{j=1}^{n_R} \hat{H}_{R,j} + K_1^{TM}(T) \sin^2 \theta^{TM} - M^{TM}(T) \cdot B, \]

where \( \hat{H}_{R,j} \) is a Hamiltonian for R ion on j-th site and \( n_R \) is the number of R ion in the unit cell volume \( V_0 \). Second and third term represent the phenomenological treatment of MA energy and Zeeman term on TM sublattice, where \( K_1^{TM}(T) \) and \( M^{TM}(T) \) are the temperature dependent anisotropy constant and magnetization vector of TM sublattice, respectively, and \( \theta^{TM} \) is the polar angle of \( M^{TM}(T) \) against the c-axis. \( M^{TM}(T) \) is given as \( M^{TM}(T)e^{TM} \) by using the absolute value of the sublattice magnetization \( M^{TM}(T) \) and a directional vector \( e^{TM} \) of \( M^{TM}(T) \). \( M^{TM}(T) \) is defined by a part of magnetization subtracting the 4f electron contribution from the total magnetization. \( B \) is an applied field.

A. Hamiltonian of Single R Ion

The Hamiltonian for 4f shell in j-th R ion in Eq. (1) is

\[ \hat{H}_{R,j} = \sum_{i=1}^{n_{4f}} \hat{h}_j(i) + \frac{1}{8\pi\varepsilon_0} \sum_{j' \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_{i'}|}, \]

with

\[ \hat{h}_j(i) = \hat{\xi}_i \cdot \hat{s}_i + 2\mu_B \hat{s}_i \cdot B_{ex,j}(T) + \int r_i^2 |R_{4f}(r_i)|^2 V_j(r_i)dr_i + \mu_B(\hat{\xi}_i + 2\hat{s}_i) \cdot B. \]

The first and second terms in Eq. (2) represent the single electron contribution and the electron-electron repulsion in 4f shell, respectively, where \( n_{4f} \) is the number of 4f electrons, \( \varepsilon_0 \) and \( e \) are the vacuum permittivity and the elementary charge, respectively. \( \hat{h}_j(i) \) in Eq. (3) is the Hamiltonian for i-th 4f electron on j-th R site, where the first term in Eq. (3) is the spin-orbit interaction (SOI) between spin (\( \hat{s}_i \)) and orbital (\( \hat{\xi}_i \)) angular momenta, with a coupling constant \( \xi \). The second term represents the exchange interaction between spin moment and temperature dependent exchange field \( B_{ex,j}(T) = -e^{TM}B_{ex,j}(T) \).
on $j$-th $R$ site, where $\mu_B$ is the Bohr magneton. The third and fourth terms are the CF and Zeeman terms, respectively. In the expression of CF, $V_j(r_i)$ and $R_{4f}(r_i)$ are Coulomb potential and radial parts of the $4f$ wave function on $j$-th $R$ site, respectively. Note that the kinetic energy and screened central potential terms are effectively taken into account in the formation of $4f$ orbital.

To obtain the electronic properties at $T = 0$, we apply the first-principles and determine the parameters in the Hamiltonians in Eq. (3). We use the full-potential linearized augmented plane wave plus local orbitals (APW+lo) method implemented in the WIEN2k code. The Kohn-Sham equations are solved within the generalized-gradient approximation (GGA). To simulate localized $4f$ states, we treat $4f$ states as atomic-like core states, which is so called opencore method.

We calculate the ground state properties of SmFe$_{12}$ such as Coulomb potential, charge distribution, and sublattice magnetizations. In accord with the previous theoretical studies for SmFe$_{12}$, we assume that Sm ion has trivalent-like electronic structure. The exchange fields $B_{\text{ex}}$ in Eq. (3) at $T = 0$ are determined from an energy increase caused by spin flip of $4f$ electrons, and CFs acting on $i$-th $4f$ electron are directly estimated from Coulomb potential $V_j(r_i)$ acting on $j$-th $R$ site. It is noted that the single ion Hamiltonian $H_{R,j}$ thus determined for $j$-th $R$ ions includes effects of $TM$ atoms surrounding the $R$ ions as a mean field.

Practically, the CF term is rewritten as the following formula,

$$\int_0^{r_c} r_i^2 |R_{4f}(r_i)|^2 V_j(r_i) dr_i = \sum_{l,m} A_{l,j}^{m}(r_i^l) a_{l,m}^{m} (\hat{\theta}_i, \hat{\varphi}_i),$$

(4)

$$A_{l,j}^{m}(r_i^l) = a_{l,m} \int_0^{r_c} dr_i r_i^2 |R_{4f}(r_i)|^2$$

$$\times \int d\Omega_i V_j(r_i) t^m_l (\hat{\theta}_i, \hat{\varphi}_i),$$

(5)

where $A_{l,j}^{m}(r_i^l)$ is CF parameter on $j$-th $R$ site, $a_{l,m}$ is a numerical factor, $t^m_l (\hat{\theta}_i, \hat{\varphi}_i)$ is tesseral harmonic function of a solid angle $\Omega = (\hat{\theta}_i, \hat{\varphi}_i)$, and $r_c$ is a cut-off radius.

Values of CF parameters $A_{l,j}^{m}(r_i^l)$ in Eq. (4), exchange field $B_{\text{ex}}(0)$ in Eq. (3), $TM$-sublattice magnetization $M_{TM}(0)$ in Eq. (4) in SmFe$_{12}$ are shown in TABLE. The lattice constants used in these calculations are the experimental values $a = b = 8.35$ Å and $c = 4.8$ Å. For Wycoff positions, we apply the theoretically optimized ones given in Ref. We here apply the concept of LS coupling to the single electron Hamiltonian of Eq. (3) with Russell Saunders states $|L, S; J, M\rangle$, due to the strong Coulomb interaction between $4f$ electrons. According to the Hund’s rule, we specify the quantum number of total orbital (spin) moment $L(S)$. Total angular momentum $J$ is varied from $|L - S|$ to $L + S$, and $M$ is the magnetic quantum number. Thus the single ion Hamiltonian in Eq. (2) can be reduced to:

$$\hat{H}_R = \hat{H}_{\text{so}} + \hat{H}_{\text{ex}} + \hat{H}_{\text{CF}} + \hat{H}_Z,$$

(6)

$$\hat{H}_{\text{so}} = \hat{\mathbf{L}} \cdot \hat{\mathbf{S}},$$

(7)

$$\hat{H}_{\text{ex}} = 2 \mu_B \mathbf{S} \cdot \mathbf{B}_{\text{ex}}(T),$$

(8)

$$\hat{H}_{\text{CF}} = \sum_{l,m} B_{l,m}^{m} \Theta_l^{m} C_{l,j}^{m}(\hat{\mathbf{L}}),$$

(9)

$$\hat{H}_Z = \mu_B (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B}.$$ 

(10)

Hereafter, the site index $j$ is omitted for single-ion quantity. $\mathbf{L}$ and $\mathbf{S}$ are total orbital and spin momenta of $4f$ electrons, respectively, $B_{l,m}^{m} = \frac{1}{\sqrt{(2l + 1)/4\pi}} \frac{2l + 1}{a_{l,m}} a_{l,m}^{m}$ and $B_{l,m}^{m} = \frac{1}{\sqrt{(2l + 1)/8\pi}} a_{l,m}^{m}$ for $l \neq 0$, and $\Theta_l^{m} = \langle L \parallel \sum_{l} C_{l,j}^{m}(\hat{\theta}_i, \hat{\varphi}_i) \parallel L \rangle / \langle L \parallel \sum_{l} C_{l,j}^{m}(\hat{\theta}_i, \hat{\varphi}_i) \parallel L \rangle$. In the treatment of SOI, we should note that the eigenstates of LS coupling are specified by the quantum number of $J$. In general, the term $H_{\text{so}}$ is dominating in Eq. (6). Thus $J$ is a good quantum number in most of the $R$-$4f$ systems. Because the LS coupling in Sm compounds is weak compared with other $R$ ones, it is necessary to include excited $J$-multiplets. Hereafter, we abbreviate the states $|L, S; J, M\rangle$ as $|J, M\rangle$.

**B. Single $R$ Ion Hamiltonian in LS Coupling Regime**

We here apply the concept of LS coupling to the single electron Hamiltonian of Eq. (3) with Russell Saunders states $|L, S; J, M\rangle$, due to the strong Coulomb interaction between $4f$ electrons. According to the Hund’s rule, we specify the quantum number of total orbital (spin) moment $L(S)$. Total angular momentum $J$ is varied from $|L - S|$ to $L + S$, and $M$ is the magnetic quantum number. Thus the single ion Hamiltonian in Eq. (2) can be reduced to: 

$$\hat{H}_R = \hat{H}_{\text{so}} + \hat{H}_{\text{ex}} + \hat{H}_{\text{CF}} + \hat{H}_Z,$$

(6)

$$\hat{H}_{\text{so}} = \hat{\mathbf{L}} \cdot \hat{\mathbf{S}},$$

(7)

$$\hat{H}_{\text{ex}} = 2 \mu_B \mathbf{S} \cdot \mathbf{B}_{\text{ex}}(T),$$

(8)

$$\hat{H}_{\text{CF}} = \sum_{l,m} B_{l,m}^{m} \Theta_l^{m} C_{l,j}^{m}(\hat{\mathbf{L}}),$$

(9)

$$\hat{H}_Z = \mu_B (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B}.$$ 

(10)

Hereafter, the site index $j$ is omitted for single-ion quantity. $L$ and $S$ are total orbital and spin momenta of $4f$ electrons, respectively, $B_{l,m}^{m} = \frac{1}{\sqrt{(2l + 1)/4\pi}} \frac{2l + 1}{a_{l,m}} a_{l,m}^{m}$ and $B_{l,m}^{m} = \frac{1}{\sqrt{(2l + 1)/8\pi}} a_{l,m}^{m}$ for $l \neq 0$, and $\Theta_l^{m} = \langle L \parallel \sum_{l} C_{l,j}^{m}(\hat{\theta}_i, \hat{\varphi}_i) \parallel L \rangle / \langle L \parallel \sum_{l} C_{l,j}^{m}(\hat{\theta}_i, \hat{\varphi}_i) \parallel L \rangle$. In the treatment of SOI, we should note that the eigenstates of LS coupling are specified by the quantum number of $J$. In general, the term $H_{\text{so}}$ is dominating in Eq. (6). Thus $J$ is a good quantum number in most of the $R$-$4f$ systems. Because the LS coupling in Sm compounds is weak compared with other $R$ ones, it is necessary to include excited $J$-multiplets. Hereafter, we abbreviate the states $|L, S; J, M\rangle$ as $|J, M\rangle$.

**FIG. 2. Energy levels as a function of $B_{\text{ex}}(T)/B_{\text{ex}}(0)$ of the Sm-$4f$ states in SmFe$_{12}$ at $e_{TM} = n_c$ and for $\mathbf{B} = 0$. High energy levels originated from $J = 13/2$ and $J = 15/2$ multiplets are above 6000 K, which are not shown.**

The energy levels of Sm-$4f$ states in SmFe$_{12}$ depend on $B_{\text{ex}}(T)$ and applied field $\mathbf{B}$. Fig. 2 shows the $B_{\text{ex}}(T)/B_{\text{ex}}(0)$ dependence of the energy levels for $e_{TM} = n_c$, which is a unit vector parallel to $c$-axis, and
for \( B = 0 \). The data needed are given in TABLE I. As for SOI constant, we use experimental value of \( \lambda/k_B = \xi/5k_B = 411 \text{ K}^4 \). At \( B_{\text{ex}}(T) = 0 \) the \( s \) is strongly coupled with \( L \) to form a Kramers doublet with a total angular momentum \( J \) due to the large \( LS \) coupling with fine CF splitting. With increasing \( B_{\text{ex}}(T)/B_{\text{ex}}(0) \), the exchange field breaks the time-reversal symmetry and lift the degeneracy.

C. Phenomenological Model for TM Sublattice

For finite temperature magnetic properties of TM, we apply a phenomenological formula assuming uniform \( M_{\text{T}}(T) \) and \( K_T(T) \). For \( M_{\text{T}}(T) \), we apply the Kuzmin formula:  

\[
\frac{M_{\text{T}}(T)}{M_{\text{T}}(0)} = \frac{B_{\text{ex}}(T)}{B_{\text{ex}}(0)} = \alpha(T),
\]

\[
\alpha(T) = \left[ 1 - s \left( \frac{T}{T_C} \right)^{3/2} - (1 - s) \left( \frac{T}{T_C} \right)^{5/2} \right]^{1/3},
\]

where \( T_C \) is Curie temperature and \( s \) is a fitting parameter. The temperature dependence of \( K_T(T) \) has been expressed by an extended power law:  

\[
\frac{K_T(T)}{K_T(0)} = \alpha^3(T) + \frac{8}{7} C_1 \left[ \alpha^3(T) - \alpha^{10}(T) \right] + \frac{8}{7} C_2 \left[ \alpha(T)^3 - \frac{18}{11} \alpha(T)^{10} + \frac{7}{11} \alpha(T)^{21} \right],
\]

where \( C_1 \) and \( C_2 \) are fitting parameters.

In present study for SmFe\(_{12}\) compound, we use values of \( s = 0.01 \) and \( T_C = 555 \text{ K} \) in Eq. (12), as used by Hirayama et al. They showed that the magnetization agrees well with experimental measurement for SmFe\(_{12}\). The values of \( C_1, C_2 \) and \( V_0 K_{\text{T}}(0) \) in Eq. (13) are determined as \(-0.263, -0.237 \) and \( 47.7 \text{ K} \), respectively, by fitting the expression to observed data for YFe\(_{11}\)Ti in Ref. 10.

### III. METHOD OF MODEL CALCULATIONS

A. Statistical Method

To calculate the finite temperature magnetic properties, we use the model Hamiltonian and calculate MA and magnetic moment for Sm 4\textit{f} electrons using the statistical method for the partial system. Using the eigenvalues of the Hamiltonian Eq. (6), we express the free energy density as,

\[
G(e^{\text{T}}, T, B) = \frac{1}{V_0} \sum_{j=1}^{n_R} \ln \left[ \frac{Z_j(e^{\text{T}}, T, B)}{Z_j(1, e^{\text{T}}, T, B)} \right] + \sum_{n=1}^{q} \left[ E_{n,j}(e^{\text{T}}, T, B) \right],
\]

where \( g_j(e^{\text{T}}, T, B) \) is Gibbs free energy for \( R \)-4\textit{f} partial system, \( E_{n,j}(e^{\text{T}}, T, B) \) and \( Z_j(e^{\text{T}}, T, B) \) are the eigenvalue and the partition function of \( j \)-th \( R \) Hamiltonian \( H_{R,j} \) [Eq. (10)] for given \( e^{\text{T}} \), respectively. The direction of the TM magnetization \( e^{\text{T}} \) is treated as an external parameter. The equilibrium condition of the system for given \( T \) and \( B \) is:

\[
G(e^{\text{T}}, T, B) = \min_{e^{\text{T}}} G(e^{\text{T}}, T, B),
\]

where \( e^{\text{T}} \) is the direction of TM sublattice magnetization in the equilibrium. In practice, we determine the minimal \( G(e^{\text{T}}, T, B) \) numerically by changing \( e^{\text{T}} \).

The MA energy is given by the free energy \( G(e^{\text{T}}, T, 0) \) with different directional vector \( e^{\text{T}} \). In the tetragonal symmetry, \( g_j(e^{\text{T}}, T, 0) \) in \( G(e^{\text{T}}, T, 0) \) is formally expressed as:

\[
g_j(e^{\text{T}}, T, 0) = \sum_{p=1}^{\infty} \left[ k_{p,0}(T) + \sum_{q=1}^{[p/2]} k_{p,q}(T) \cos(4\vartheta^{\text{T}}) \right] \times \sin^{2p} \vartheta^{\text{T}} + C(T),
\]

where \( \vartheta^{\text{T}} \) and \( \varphi^{\text{T}} \) are polar and azimuthal angle of \( e^{\text{T}} \) respectively, \( [p/2] \) indicates the greatest integer of \( p/2 \), and \( k_{p,0}(T) \) and \( k_{p,q}(T) \) are out-of-plane and in-plane MA constant for \( j \)-th \( R \) ion. The \( C(T) \) is an angle independent constant. The series expansion does

| TABLE I. Values of CF potentials \( A_{i,j}^n(r^2) \) [K], exchange field \( \mu_B B_{\text{ex},j}(0)/k_B \) [K], and TM-sublattice magnetization \( V_0 M_{\text{T}}(0) \) [\( \mu_B \)] in SmFe\(_{12}\) calculated by first-principles, where \( \mu_B \) and \( k_B \) are Bohr magneton and Boltzmann constant, respectively, and \( V_0 = a \times b \times c \). We note that \( A_{i,j}^n(r^2) \) and \( \mu_B B_{\text{ex},j}(0)/k_B \) are independent of site index \( j \). |
|---|---|---|---|---|---|---|
| \( A_{i,j}^n(r^2) \) | \( A_{i,j}^4(r^4) \) | \( A_{i,j}^4(r^4) \) | \( A_{i,j}^4(r^6) \) | \( A_{i,j}^4(r^6) \) | \( \mu_B B_{\text{ex},j}(0)/k_B \) | \( V_0 M_{\text{T}}(0) \) |
| -71.4 | -21.3 | -49.3 | 5.9 | 3.0 | 296.1 | 51.6 |
not guarantee the convergence, however, for finite \( p \), \( k_{p,j}(T) \) can be obtained from the comparison between the Taylor series of \( g_j(e^{TM}, T, 0) \) of Eqs. (11) and (15) with respect to \( \theta^{TM} \) for a fixed \( \varphi^{TM} \) as:

\[
g_j(e^{TM}, T, 0) = g_j(0) + g_j(1)(\theta^{TM})^2 + \cdots
\]

respectively, which are resulting in

\[
k_{1,j}(T) = \frac{1}{2} g_j(2)(T),
\]

\[
k_{2,j}(T) = \frac{1}{3} k_{1,j}(T) + \frac{1}{4!} g_j(4)(T),
\]

etc. Using MA energy on the single \( R \) ion in Eq. (18), the total MA constants are obtained as

\[
K_1(T) = \frac{1}{V_0} \sum_{j=1}^{n_R} k_{1,j}(T) + K_1^{TM}(T), \quad (p = 1),
\]

\[
K_p^{(q)}(T) = \frac{1}{V_0} \sum_{j=1}^{n_R} k_{p,j}^{(q)}(T), \quad (p \geq 2),
\]

where \( K_p(T) \) and \( K_p^{(q)}(T) \) are out-of-plane and in-plane MA constant in whole system.

The orbital and spin components of the magnetic moment of a single \( R \) ion in the equilibrium, can be calculated by:

\[
m_{L,j}(T, B) = -\mu_B \sum_{n} \rho_{n,j}(T, B) \langle n, j|L|n, j\rangle,
\]

\[
m_{S,j}(T, B) = -2\mu_B \sum_{n} \rho_{n,j}(T, B) \langle n, j|S|n, j\rangle,
\]

respectively, where

\[
\rho_{n,j}(T, B) = \exp \left[ -\beta E_{n,j}(e_0^{TM}, B) \right] / Z_j(e_0^{TM}, T, B)
\]

is the \( n \)-th eigenstate for \( E_{n,j}(e_0^{TM}, B) \), and the total magnetization \( M_s(T, B) \) is given as

\[
M_s(T, B) = \frac{1}{V_0} \sum_{j=1}^{n_R} m_j(T, B) + M^{TM}(T)e_0^{TM},
\]

with \( m_j(T, B) = m_{L,j}(T, B) + m_{S,j}(T, B) \).

Finally, to confirm the convergence of the probability weights for excited-\( J \) multiplet states at \( B = 0 \), we define a following weight function:

\[
W_J(T) = \sum_{n,M} \rho_{n,j}(T, 0)|\langle n, j|J, M\rangle|^2.
\]

In the case of SmFe\(_{12}\) crystal, the value of \( W_J(T) \) is independent of site index \( j \). The results are shown in TABLE II which indicates good convergence of weight for the number of the excited \( J \)-multiplets even at \( T = T_C = 555 \) K. Thus in the calculation using statistical method for SmFe\(_{12}\), we take the excited \( J \)-multiplets up to \( J = 9/2 \).

In the analytical calculation, the \( J \)-mixing effects are approximately treated only for the lowest-\( J \) multiplet by using unitary transformation.

### B. Analytical Method

According to hierarchy of energy scale in \( R \) intermetallic compounds: \( \hat{H}_{so} \gg \hat{H}_{ex} \gg \hat{H}_{CF} \sim \hat{H}_Z \), we develop an analytical method for finite temperature magnetic properties, which enables us to connect the thermodynamic properties directly to our model parameters based on electronic states. Practically, we generalize the analytical expression of Gibbs free energy\(^{25,26,27} \) to include the effects of \( J \)-mixing using a first-order perturbation for the CF potential and Zeeman energy. We also derive an analytical expression for the magnetization curve, which enables us to estimate the CF potential using the observed results. The procedure of the formalism consists of (i) construction of starting Hamiltonian for single \( R \) ion, (ii) approximation for diagonal matrix element of an effective Hamiltonian, (iii) finite temperature perturbation for single \( R \) ion, and (iv) thermodynamic analysis.

#### 1. Effective Lowest-\( J \) Multiplet Hamiltonian for Single \( R \) Ion

To restrict \( \hat{H}_R \) in low-energy subspace for \( \hat{H}_{so} \gg \hat{H}_{ex} \), the effective lowest-\( J \) multiplet Hamiltonian \( \hat{H}_R^{\text{eff}} \) is obtained by unitary transformation and projection, where the off-diagonal matrix elements between inter-\( J \) multiplets become negligibly small, and compensating term \( \hat{H}_{\text{mix}} \) is added in diagonal element for lowest-\( J \) multiplet. We here introduce modified version of effective Hamiltonian as explained below.

First, we define a rotational operator \( \hat{D}(e^{TM}) \) which transforms the quantization axis to \( e^{TM} \). With this operator, the Hamiltonian \( \hat{H}_R \) and \( \hat{H}_A \ (A = \text{ex}, \text{CF} \text{ and } Z) \) is transformed to:

\[
\hat{D}^\dagger(e^{TM})\hat{H}_R\hat{D}(e^{TM}) = \hat{H}_R' + \hat{H}_{\text{ex}}' + \hat{H}_{\text{CF}}' + \hat{H}_Z',
\]
\[ \hat{\mathcal{H}}_{\text{so}}' = \frac{\lambda}{2} \left( \hat{J}^2 - L(L+1) - S(S+1) \right), \]
\[ \hat{\mathcal{H}}_{\text{ex}}' = -2B_{\text{ex}}(T)C_{0}^{(1)}(\hat{S}), \]
\[ \hat{\mathcal{H}}_{\text{CF}} = \sum_{l,m,m'} B_{m}^{\alpha}(D_{m,m'}^{(l)}(e^{TM}))^* C_{m}^{(l)}(\hat{L}), \]
\[ \hat{H}_{Z} = \mu_{B} \sum_{m,m'} b_{m}^{(l)}(P_{m,m'}(e^{TM}))^* \left[ C_{m}^{(l)}(\hat{L}) + 2C_{m}^{(l)}(\hat{S}) \right], \]

where \( \hat{J} = \hat{L} + \hat{S} \), \( C_{m}^{(l)}(\hat{A}) \) is the spherical tensor operator with rank \( k \) for angular momentum \( \hat{A} \), and \( b_{m}^{(l)} \) is a magnetic field tensor: \( b_{0}^{(l)} = B_{z} \) and \( b_{\pm 1}^{(l)} = -(\pm B_{x} \pm i B_{y})/\sqrt{2} \). \( D_{m,m'}^{(l)}(e^{TM}) = D_{m,m'}^{(l)}(\varphi^{TM}, \theta^{TM}, 0) \) is the Wigner's D function. Now we apply a unitary transformation (Schrieffer-Wolf transformation) to \( \hat{\mathcal{H}}_{R}' \),

\[ e^{i\Omega} \hat{\mathcal{H}}_{R}' e^{-i\Omega} = \hat{\mathcal{H}}_{R}' + i \left[ \hat{\Omega}, \hat{\mathcal{H}}_{R}' \right] + O(\Omega^2), \]

and introduce a projection operator \( \hat{P}_{J} = \sum_{J=-J}^{J} |J, M\rangle \langle J, M| \), by which the space of the \( J \)-multiplet is restricted to the lowest one. The operator \( \hat{\Omega} \) is defined so as to remove the first-order off-diagonal matrix elements for \( J \) in \( \hat{\mathcal{H}}_{R}' \):

\[ i \sum_{J'} \left[ \hat{\Omega}, \hat{P}_{J'} \hat{\mathcal{H}}_{R}' \hat{P}_{J'} \right] = \sum_{J'} \hat{P}_{J'} \hat{\mathcal{H}}_{R}' \hat{P}_{J'} - \hat{\mathcal{H}}_{R}'. \]

Apparently, \( \langle J, M|\hat{\mathcal{H}}_{R}'|J', M'\rangle = 0 \). The second term of the right-hand-side of Eq. \( \text{(33)} \) has now a diagonal matrix with corrections to the diagonal elements in the original \( \hat{\mathcal{H}}_{R}' \). The second and higher-order terms in \( \hat{\Omega} \) are neglected. By inserting Eq. \( \text{(33)} \) to Eq. \( \text{(32)} \), we obtain

\[ \hat{\mathcal{H}}_{R}^{\text{eff},J} = \hat{\mathcal{H}}_{R} + i \left[ \hat{\Omega}, \hat{\mathcal{H}}_{R} \right], \]
\[ \hat{\mathcal{H}}_{R}^{J} = \hat{\mathcal{H}}_{R} + \hat{\mathcal{H}}_{\text{mix}}^{J}, \]
\[ \hat{\mathcal{H}}_{\text{mix}}^{J} = \frac{1}{2} \hat{P}_{J} \left[ \hat{\Omega}, \hat{\mathcal{H}}_{R} \right] \hat{P}_{J}, \]

where \( E_{J} = \lambda[J(J+1) - L(L+1) - S(S+1)]/2 \) and \( \hat{\mathcal{H}}_{R}^{J} = \hat{\mathcal{P}}_{J} \hat{\mathcal{H}}_{R} \hat{\mathcal{P}}_{J} \) (\( A=\text{ex}, \text{CF} \) and \( F \)). We here classify analytical models depending on the approximation to the matrix element of \( \hat{\Omega} \) for \( J \neq J' \) in Eq. \( \text{(33)} \) as follows:

- **model A**: Lowest-\( J \) multiplet without mixing as:
  \[ \langle J, M|\hat{\mathcal{H}}^{A}|J', M'\rangle = 0, \]

- **model B**: Effective lowest-\( J \) multiplet with mixing as:
  \[ \langle J, M|\hat{\mathcal{H}}^{B}|J', M'\rangle = i \frac{\langle J, M|\hat{\mathcal{H}}_{1}|J', M'\rangle}{E_{J'} - E_{J}}, \]

- **model C**: Modified effective lowest-\( J \) multiplet with mixing (present study) as:
  \[ \langle J, M|\hat{\mathcal{H}}^{C}|J', M'\rangle = i \frac{\langle J, M|\hat{\mathcal{H}}_{1}|J', M'\rangle}{E_{J'} - E_{J}} \]
  \[ \times \sum_{M''} \left[ \langle J, M|\hat{\mathcal{H}}_{1}|J', M''\rangle \langle J', M''|\hat{\mathcal{H}}_{1}|J', M'\rangle \right] - \langle J, M|\hat{\mathcal{H}}_{1}|J, M'\rangle \langle J, M'|\hat{\mathcal{H}}_{1}|J', M'\rangle, \]

where \( \hat{\mathcal{H}}_{1} = \hat{\mathcal{H}}_{R}' - \hat{\mathcal{H}}_{\text{so}}' \). The approximations are referred to as model A, B and C, hereafter. By using \( \hat{\Omega}^{B} \), Magnani et al. derived the effective lowest-\( J \) multiplet Hamiltonian\( ^{29} \) and Kuz'min had also derived an equivalent approximation for anisotropy constants\( ^{28} \). In the latter work, it was pointed out that the approximations of the models A and B are not applicable to the Sm compounds due to relatively small \( \lambda \). In the present study, we have modified \( \hat{\Omega}^{B} \) to \( \hat{\Omega}^{C} \).

### 2. Approximation for Diagonal Matrix Element of \( \hat{\mathcal{H}}_{R}^{\text{eff},J} \)

The energy levels for \( 4f \) electron system are obtained by the exact diagonalization of \( \hat{\mathcal{H}}_{R} \) in Eq. \( \text{(1)} \), and the diagonal matrix elements of \( \hat{\mathcal{H}}_{R}^{\text{eff},J} \) can be expressed as:

\[ \langle J, M|\hat{\mathcal{H}}_{R}^{\text{eff},J}|J, M\rangle = \langle J, M|\hat{\mathcal{H}}_{R}'|J, M\rangle + \langle J, M|\hat{\mathcal{H}}_{\text{mix}}^{J}|J, M\rangle, \]

through two unitary transformations by \( \hat{D}(e^{TM}) \) and \( e^{-i\hat{\Omega}} \). The first term in Eq. \( \text{(37)} \) can be obtained by using the relation \( D_{m,m'}^{(l)}(\varphi^{TM}, \theta^{TM}, 0) = Y_{l}^{m}(\varphi^{TM}, \theta^{TM}) \) and Wigner Eckert theorem\( ^{50} \).

\[ \langle J, M|\hat{\mathcal{H}}_{R}'|J, M\rangle = E_{J} - 2(g_{J} - 1)\mu_{B} B_{\text{ex}}(T) \langle J, M|C_{0}^{(1)}(\hat{J})|J, M\rangle + \sum_{l,m} A_{l}^{m}(r^{l}) \Theta_{l}^{m}(e^{TM}) \langle J, M|C_{0}^{(1)}(\hat{J})|J, M\rangle \]

\[ + \mu_{B} g_{J} (e^{TM} \cdot \mathbf{B}) \langle J, M|C_{0}^{(1)}(\hat{J})|J, M\rangle, \]

where \( \Theta_{l}^{m} \) is the Stevens factor\( ^{46,53} \). By using the model C with \( \hat{\Omega}^{C} \), the second term in Eq. \( \text{(37)} \) is approximated as:

\[ \langle J, M|\hat{\mathcal{H}}_{\text{mix}}^{J}|J, M\rangle \sim - \frac{1}{\Delta_{\text{so}}} \langle J, M|\hat{\mathcal{H}}_{\text{ex}}'|J + 1, M\rangle \times \langle J + 1, M|\hat{\mathcal{H}}_{\text{ex}}'|J + 1, M\rangle + 2 \hat{H}_{C} + 2 \hat{H}_{Z}|J, M\rangle \]

\[ \times \left[ 1 - \frac{\langle J + 1, M|\hat{\mathcal{H}}_{\text{ex}}'|J + 1, M\rangle - \langle J, M|\hat{\mathcal{H}}_{\text{ex}}'|J, M\rangle}{\Delta_{\text{so}}} \right], \]

\[ \text{(39)} \]
where $\Delta_{so} = \lambda(J + 1)$. Contributions from $\hat{H}_{CF}$ and $\hat{H}_Z$ are neglected in the second term of the square bracket. By using Wigner-Eckert theorem$^{39}$ and the relation for products of the matrix elements of the spherical tensor operators given by Eq. (5) in chapter 12. of Ref$^{39}$, the diagonal matrix element is expressed as follows:

$$
\langle J, M | \hat{H}_{mix} | J, M \rangle = -\frac{\Delta_{ex}(T)}{3S} \langle J, M | \hat{T}_{I}(J) | J, M \rangle - \sum_{l,m} A_{lm}^n \{l \} \sum_{\alpha l,m} \frac{(\epsilon^{TM})_{\alpha l,m}}{2l + 1} \langle J, M | \hat{T}_{I}(J) | J, M \rangle + (\epsilon^{TM} \cdot B) \frac{2(L + 1)}{3(J + 1)} \langle J, M | \hat{T}_{I}(J) | J, M \rangle,
$$

(40)

where $\Delta_{ex}(T) = -2(q_{J} - 1)\mu BB_{ex}(T)$. We here use the relation $J = L - S$ assuming $R$ as light rare-earth and $\Xi_{J}^l = -2J/[(3^5 \times 7 + 11) - 2^2 \times 17/(3^5 \times 7 \times 11^2)$] for Ce$^{3+}$ and Sm$^{3+}$, respectively, and $\Xi_{J}^l = \Theta_{J}^l$ in the other cases.

More explicit expression of $\hat{T}_{I}(J)$ depends on further approximations. So far top two approximations have been adopted: one completely neglect the term $\langle J, M | \hat{H}_{mix} | J, M \rangle$, that is, $\hat{H}_{mix} = 0$, and the other is an approximation to neglect the second term in the square bracket in Eq. (39) which was adopted by Kuz’min$^{25}$ and Magnani et al$^{29}$. According to the model approximations of $\hat{W}^X$ with $X = A, B, and C$, the quantities $\hat{T}_{I}(J)$ are denoted as $\hat{T}_{I}^{A}(J)$ with $X = A, B, and C$. Clearly $\hat{T}_{I}^{A} = 0$, and for $X = B$ and $C$,

$$
\hat{T}_{I}^{B(C)}(J) = \frac{\Delta_{ex}(T)}{\Delta_{so}} \left[ \frac{2J + l + 1}{2} \right] \cdot \left[ \frac{2}{2J + l + 2} \right] \cdot \hat{V}_{I}(J),
$$

(41)

with

$$
\hat{V}_{I}^{B} = C_{I}^{(-)}(J),
$$

$$
\hat{V}_{I}^{C} = C_{I}^{(0)}(J) + \frac{\Delta_{ex}(T)}{\Delta_{so}} \left[ \frac{L + S + 1}{2J + 2} \right] \left[ \frac{((2J - l + 1))}{4(2J + l + 1)} \right] \cdot C_{0}^{(l+1)}(J)
$$

(42)

where we formally set $C_{0}^{(l+1)}(J) = 0$.

The energy levels $E_n$ for 4f electron system, which consist of the lowest energy $E_1$ to the 2J-th excited energy $E_{2J+1}$, are now expressed as,

$$
E_{X}^{J} = \langle J, M | \hat{H}_{eff}^{X} | J, M \rangle + \langle J, M | \hat{H}_{mix}^{X} | J, M \rangle,
$$

(43)

$$(X = A, B, and C)$$

with $M = -J$ to $J$ for the model A, B, and C.

Fig. 3 shows the diagonal matrix element $E_{X}^{J}$ ($X = A, B, and C$) of the effective lowest-$J$ multiplet Hamiltonian $\hat{H}_{eff}^{A}$ at $T = 0$ in Eq. (43). Note that CF coefficients and exchange fields are determined by the first principles, and the same values are used for models A, B, and C. The results are compared with the exact results. To distinguish the contribution from each $\hat{H}_{so}$, $\hat{H}_{ex}$, and $\hat{H}_{CF}$ in $\hat{H}_{R}$ of Eq. (12), the original Hamiltonian $\hat{H}_{R}$ is taken as $\hat{H}_{so} + \hat{H}_{ex}$, or $\hat{H}_{so} + \hat{H}_{ex} + \hat{H}_{CF}$.

IV. CONCLUSION

We apply the first-order perturbation at finite temperature assuming $\hat{H}_{ex}^{J} \approx \hat{H}_{CF}^{J} + \hat{H}_{Z}^{J} + \hat{H}_{mix}^{J}$. The unperturbed and perturbed Hamiltonians are $\hat{H}_{ex}^{J} = \Delta_{ex}(T)C_{0}^{(1)}(J) \equiv \hat{H}^{(0)}$ and $\hat{H}_{CF}^{J} + \hat{H}_{Z}^{J} + \hat{H}_{mix}^{J} \equiv \hat{H}$, respectively. Note that $\hat{H}_{so}$ is effectively taken into account in the $J$-multiplet formation of the $R$ ion. The approximated Gibbs free energy for $R$-4f partial system on $j$-th $R$ site up to first-order perturbation is
formally expressed as \( g_e(T, eM, T, B) = -k_B \ln Z_0(T) + \sum_M \rho_{M}^{(0)}(T) \langle J, M | J' | J, M \rangle \), where \( E_{M}^{(0)}(T) = \Delta_{ex}(T)M \), \( Z_0(T) = \sum_M \exp[-\beta E_{M}^{(0)}(T)], \) and \( \rho_{M}^{(0)}(T) = \exp[-\beta E_{M}^{(0)}(T)]/Z_0(T) \). More explicitly, it is given as,

\[
g(e^{TM}, T, B) = k_B T \sum_M \rho_{M}^{(0)}(T) \ln \rho_{M}^{(0)}(T) + \sum_M \rho_{M}^{(0)}(T) E_M, \tag{44}
\]

by using \( E_M \) in Eq. \[43\]. It is noted that \( g(e^{TM}, T, B) \) is model dependent because \( E_M \) equals to \( E_M^{A} \), \( E_M^{B} \) or \( E_M^{C} \), corresponding to the model adopted.

By using the Zeeck free energy \( g(e^{TM}, T) \) for \( R-4f \) partial system, the Gibbs free energy in the modified effective lowest-J model is given as,

\[
g(e^{TM}, T) = \frac{f(e^{TM}, T)}{m(T)}e^{TM} \cdot B, \tag{45}
\]

\[
m(T) = \mu_B \left[ g_J B_J^2(x) - \frac{2(J + 1)}{3(2J + 1)} T_J^2(x) \right], \tag{46}
\]

with

\[
f(e^{TM}, T) = k_B T \sum_M \rho_{M}^{(0)}(T) \ln \rho_{M}^{(0)}(T) + f_{ex}(T) + f_{CF}(e^{TM}, T), \tag{47}
\]

\[
f_{ex}(T) = -\Delta_{ex}(T) \left[ J B_J^2(x) + \frac{J + 1}{2J + 1} T_J^2(x) \right], \tag{48}
\]

\[
f_{CF}(e^{TM}, T) = \sum_{l,m} A_{l,m}^{(TM)} \Xi_{l,m}^{TM} \frac{t_{l,m}}{a_{l,m}} \times \left[ J B_J^l(x) + \frac{(l + 1)}{2J + 1} T_J^l(x) \right]. \tag{49}
\]

Here \( x = T \Delta_{ex}(T)/k_B T \), and the model dependence appears in \( T_J^l(x) \), which is denoted as \( T_{J}^{l,X}(x) \) with \( X=A, B \) or \( C \). For \( X=A \), \( T_{J}^{l,A}(x) = 0 \) and for \( X=B \) and \( C \),

\[
T_{J}^{l,B,C}(x) = \frac{\Delta_{ex}(T)}{\Delta_{so}} \left[ \frac{2J + l + 1}{2} V_{J}^{l-1,B,C}(x) - \frac{2}{2J + l + 2} V_{J}^{l+1,B,C}(x) \right], \tag{50}
\]

with

\[
V_{J}^{l,B}(x) = J B_J^l(x), \tag{51}
\]

\[
V_{J}^{l,C}(x) = J B_J^l(x) - \frac{\Delta_{ex}(T)}{\Delta_{so}} \frac{L + S + 1}{S(J + 2)} \left[ \frac{(l J - l + 1)(l J + l + 1)}{4(2J + 1)} J_{J-1}^l B_J^{l-1}(x) \right.
\]

\[
\left. + \frac{l + 1}{2l + 1} J_{J+1}^l B_J^{l+1}(x) \right], \tag{52}
\]

where \( B_J^l(x) \) is the generalized Brillouin function \[24\] defined by

\[
(-1)^l J B_J^l(x) = \langle C_0^{(l)}(J) \rangle_0 \] with \( x = J \Delta_{ex}(T)/k_B T \) for \( l \geq 0 \), where \( \langle \hat{A} \rangle_0 = \sum_M \rho_{M}^{(0)}(T) \langle J, M | \hat{A} | J, M \rangle \). The analytical expression of \( B_J^l(x) \) is given in Ref. 5 and \( T_J^{l,A}(x) = 0, T_J^{l,B}(x) \) and \( T_J^{l,C}(x) \) are linear combination of \( B_J^{l+1}(x) \), \( B_J^{l-1}(x) \), \( B_J^{l+2}(x) \), \( B_J^{l+2}(x) \), and \( B_J^{l+2}(x) \), respectively, as shown in Eq. \[50\].

Because of the first-order perturbation for \( \hat{H}_2 \), an analytical expression of the magnetic moment \( m(T) \) is obtained as

\[
m_L(T) = m_L(T) + m_S(T), \tag{53}
\]

\[
m_S(T) = -2 \mu_B \left[ \frac{S}{J + 1} B_J^2(x) + \frac{2(L + 1)}{3(2J + 1)} T_J^2(x) \right], \tag{54}
\]

where \( m_L(T) \) and \( m_S(T) \) are orbital and spin component of magnetic moment on the \( R \) ion. It is noted that \( m_L(T) \) and \( m_S(T) \) are model dependent because of the model dependence of \( T_J^l(x) \) as shown above.

Within the finite temperature perturbation theory, the angular \( e^{TM} \) dependent part of single \( R \) ion free energy \( f(e^{TM}, T) \) in Eq. \[47\] with the tetragonal symmetry can be written by:

\[
f(e^{TM}, T) = k_1(T) \sin^2 \theta + \frac{k_2(T) + k_2(T)}{3} \cos 4 \varphi_{TM} \sin^4 \theta_{TM} + k_3(T) + \frac{k_3(T)}{3} \cos 4 \varphi_{TM} \sin^6 \theta_{TM} + C(T), \tag{55}
\]

which is a truncated form of \( g(e^{TM}, T, 0) \) in Eq. \[13\]. The \( C(T) \) is an angle independent constant. For example, the leading anisotropy constants for a trivalent magnetic light \( R \) ion (Ce\textsuperscript{3+}, Pr\textsuperscript{3+}, Nd\textsuperscript{3+}, Pm\textsuperscript{3+}, and Sm\textsuperscript{3+}) can be written as follows:

\[
k_1(T) = -3 \left[ J^2 B_J^2(x) + \frac{6}{5} T_J^2(x) \right] A_2^{(r)}(r^2) \Xi_{2}, \tag{56}
\]

\[
-40 \left[ J^4 B_J^4(x) + \frac{20}{9} T_J^4(x) \right] A_4^{(r^4)} \Xi_{4}, \tag{57}
\]

\[
-168 \left[ J^6 B_J^6(x) + \frac{42}{13} T_J^6(x) \right] A_6^{(r^6)} \Xi_{6}. \tag{58}
\]

\[
k_2(T) = 35 \left[ J^4 B_J^4(x) + \frac{20}{9} T_J^4(x) \right] A_2^{(r^4)} \Xi_{2}, \tag{59}
\]

\[
+ 378 \left[ J^6 B_J^6(x) + \frac{42}{13} T_J^6(x) \right] A_6^{(r^6)} \Xi_{6}. \tag{60}
\]

All terms of MA constants \( k_n(T) \) in model A,B, and C are given by linear terms with respect to \( A_{2n}^{(r^4)}(r^4) \).

We may rewrite the approximations used and adopted in the present formalism by using \( T_J^{l,X}(x) \) in Eq. \[50\] as follows:

- model A: Lowest-J multiplet without mixing as \( \Delta_{ex}(T)/\Delta_{so} = 0 \) or \( T_J^{A}(x) = 0 \).
holds between increasing temperature. Thus the
included in
where the temperature is scaled by Curie temperature
For comparison purpose, we also show the
Because
model B: Effective lowest-J multiplet with mixing
as \( \Delta_{\text{rel}}(T)/\Delta_{\text{so}} \)^2 = 0 or \( T_j^{Jj,\text{B}}(x) \) 28,29
model C: Modified effective lowest-J multiplet with
mixing as \( T_j^{Jj,\text{C}}(x) \) (present study).
At \( T = 0 \), we have found a following simple relation
holds between \( T_j^{Jj,\text{C}}(\infty) \) and \( T_j^{Jj,\text{B}}(\infty) \) as:
\[
R_j = \frac{T_j^{Jj,\text{C}}(\infty)}{T_j^{Jj,\text{B}}(\infty)} = 1 - \frac{\Delta_{\text{rel}}(0)}{\Delta_{\text{so}}} S(J + 2). \tag{58}
\]
Because \( R_j \) is independent of \( l \), relations among the models \( X=A, B, \) and \( C \) on \( m_{L,S}^J(0) \) and \( k_j^{(q)A}(0) \) can be
generally expressed as follows:
\[
m_{L,S}^J(0) = m_{L,S}^A(0) + R_j \left[ m_{L,S}^B(0) - m_{L,S}^A(0) \right], \tag{59}
\]
\[
k_p^{(q)A}(0) = k_p^{(q)B}(0) - k_p^{(q)A}(0). \tag{60}
\]
At finite temperatures, \( T_j^{Jj,\text{B}(\infty)}(x) \) for \( J = 5/2 \) scaled by \( T_j^{Jj,\text{B}}(\infty) > 0 \) are shown in Fig. 4(a) for the SmFe12
compound. Here, \( \Delta_{\text{rel}}(T)/\Delta_{\text{so}} \) is taken to be 0.2060\( \alpha(T) \). For comparison purpose, we also show the \( B_j^l(x)/B_j^l(\infty) \)
in Fig. 4(b). \( B_j^l(x) \) decays faster than \( T_j^{Jj,\text{B}(\infty)}(x) \) with increasing temperature. Thus the J-mixing effects
included in \( T_j^{Jj,\text{B}(\infty)}(x) \) remain even at high temperatures.

4. Thermodynamic Analysis

Finally we investigate the thermodynamical instability
by using the thermodynamic relation between Gibbs
and Helmholtz free energy, which explicitly contains the
CF potentials and the exchange field determined by first
principles. We have to note that above the room
temperature the exchange contribution \( \mathcal{H}_{\text{ex}} \) decreases with increasing temperature at a rate proportional to \( \alpha(T) \),
so the energy hierarchy is changed and thermal fluctua-
tion effects have to be considered as \( k_B T \gg \mathcal{H}_{\text{CF}} \sim \mathcal{H}_{\text{ex}} \).
Even in this case, the formulation derived here based on
generalized Brillouin function holds as shown by Kuz’min
in Refs. 26,28. In this thermodynamic analysis, we use the
model C.

By applying the finite temperature perturbation the-
ory to the lowest-J multiplet Hamiltonian, the approxi-
mated Gibbs free energy density for whole system can be
expressed as:
\[
G(e^{TM}, T, B) = F(e^{TM}, T) - M_s(T) \cdot B, \tag{61}
\]
\[
F(e^{TM}, T) = 1 \frac{1}{V_0} \sum_{j=1}^{n_r} f_j(e^{TM}, T) + K_1^{TM}(T) \sin^2 \theta^{TM}, \tag{62}
\]
\[
M_s(T) = \left[ 1 \frac{1}{V_0} \sum_{j=1}^{n_r} m_j(T) + M^{TM}(T) \right] e^{TM}, \tag{63}
\]
where \( F(e^{TM}, T) \) is Helmholtz free energy density
for whole system with model C and \( f_j(e^{TM}, T) \) and
\( m_j(T) e^{TM} \) are corresponding energy for \( j \)-shell and
expectation value of magnetic moment on \( j \)-th R ion given
in Eq. 47 and Eq. 48, respectively. The temper-
itude dependence of \( G(e^{TM}, T, B) \) can be expressed as the
linear combination of the generalized Brillouin functions
for R ion \( B_j^l(J \Delta_{ex}/k_B T) \) and the tempera-
ture coefficient for \( TM \) ion \( \alpha(T) \) in Eq. 12. The equilib-
rium condition is the same as Eq. 17, where \( e^{TM} \) becomes
the direction of total magnetization in the equi-
lbrium. We can also analyze the instability of magnetic
metastable states, which are crucially important in per-
manent magnetic materials. The metastable condition is
\( \delta G(T, e^{TM}, B) > 0 \) for given \( T \) and \( B \) with \( |e^{TM}| = 1 \).

The MA constants in whole system are obtained by
combining the contribution from \( R \) sublattice in Eq. 55
with Fe sublattice same as Eqs. 21 and 22. \( K_1(T) \) can
be substituted into the so called Krömmuller equation 54,55
to obtain the coercive field
\[
B_c(T) = \alpha B_N(T) - N_{\text{eff}} M_s(T), \tag{64}
\]
\[
B_N(T) = \frac{2K_1(T)}{M_s(T)}, \tag{65}
\]
where \( B_c(T) \) and \( B_N(T) \) are coercive and nucleation
field, respectively. \( \alpha < 1 \) is microstructural parameter
and \( N_{\text{eff}} \) is local effective demagnetization factor 56. The
\( B_N(T) \) gives upper limit of \( B_c(T) \).
IV. CALCULATED RESULTS FOR SMFe_{12}

A. Valence Mechanism of Magnetic Anisotropy

We first calculate the charge density distribution and Coulomb potential at 0 K on constituent atoms of SmFe_{12} lattice (Fig. 1) using the first principles. The calculated results determine the values of CF acting on 4f electrons, the magnitude of the exchange field B_{ex}(0) acting on the J, and the magnitude of TM sublattice magnetization. These values are used for parameter values in the model Hamiltonian. The contribution to the CF from the charge density distribution inside (outside) the muffin-tine sphere radius is called "valence (lattice) contribution". If the CF is dominated by the former contribution, we call the mechanism of the MA "valence mechanism".

The charge density distributions of single R ion are approximately replaced with charge density on atomic orbitals of 6p and 5d states. To evaluate the valence contribution to CF parameters $A_0^0(r^4)(val)$, we introduce distribution parameters $\Delta n_{6p}^{(2)}$, $\Delta n_{5d}^{(2)}$, and $\Delta n_{5d}^{(4)}$ defined as,

$$\Delta n_{n'l'}^{(i)} = \frac{4\pi}{2l+1} \sum_{m'} \int d\Omega \ t_i^0(\theta, \varphi)|t_{n'l'}^{m'}(\theta, \varphi)|^2 \Omega_{n'l',m'},$$

where $\Omega$ is the solid angle and $m'$ indicates the multiple orbitals for the quantum number ($n'l'$). The shape of the function $t_i^0(\theta, \varphi)$ in Eq. (66) is given in Fig. 4(c).

The particular cases are as follows:

$$\Delta n_{6p}^{(2)} = \frac{1}{5} \left[ n_{6p,z} - \frac{1}{2} (n_{6p,x} + n_{6p,y}) \right],$$

$$\Delta n_{5d}^{(2)} = \frac{1}{7} \left[ n_{5d,z} + \frac{1}{2} (n_{5d,x} + n_{5d,y}) - (n_{5d,x^2+y^2} + n_{5d,xy}) \right],$$

$$\Delta n_{5d}^{(4)} = \frac{1}{28} \left[ n_{5d,z} - \frac{2}{3} (n_{5d,x} + n_{5d,y}) + \frac{1}{6} (n_{5d,x^2+y^2} + n_{5d,xy}) \right],$$

where $n_{n'l',m'}$ is the occupation number of the ($n'l'$, $m'$) orbital. We note that $\Delta n_{5d}^{(4)} = 0$. Valence contribution of $A_2^0(r^2)$ and $A_4^0(r^4)$ are determined as:

$$A_2^0(r^2)(val) = F^2(4f, 6p) \Delta n_{6p}^{(2)} + F^2(4f, 5d) \Delta n_{5d}^{(2)},$$

$$A_4^0(r^4)(val) = F^4(4f, 5d) \Delta n_{5d}^{(4)},$$

with the Slater-Condon parameters:

$$F^{(2)}(4f, n'l') = \frac{e^2}{4\pi\varepsilon_0} \int_{r_<}^{r_>} \frac{r_{01}^2}{r_{01}^2 + r_{12}^2} \left| R_{4f}(r) \right|^2 d\Omega_{n'l'},$$

$$F^{(4)}(4f, n'l') = \frac{e^2}{4\pi\varepsilon_0} \int_{r_<}^{r_>} \frac{r_{01}^2}{r_{01}^2 + r_{12}^2} \left| R_{4f}(r) \right|^2 d\Omega_{n'l'} d\Omega_{n'l'},$$

where $r_< = \min(r, r')$ and $r_> = \max(r, r')$. Via Eqs. (70) and (71), the distribution parameters $\Delta n_{6p}^{(2)}$ determine $A_2^0(r^2)(val)$. It may be noted that no 6p and 5d orbitals exist for $A_6^0(r^4)(val)$.

A simple explanation for the appearance of the uniaxial MA in a Sm ion surrounded by Fe atoms is given as follows. Fig. 5(a) shows the lattice structure of SmFe_{12}. Left panel of Fig. 5(b) shows the location of Sm and Fe on (010) plane of the lattice. Because of the short atomic distance between Sm and the first nearest neighbor (n.n.) Fe(8s) sites, the distribution of valence electrons on Sm extends within the a – b plane as shown in Fig. 5(c). According to the negative sign of $\Theta_{5d}^{(0)}(\theta, \varphi)$ in Fig. 6(d), the distribution parameters determined by Eq. (66) in terms of electron numbers of 6p and 5d-orbitals are negative; $\Delta n_{6p}^{(2)} = -0.0012$, $\Delta n_{5d}^{(2)} = -0.0011$. Therefore, we obtain $A_2^0(r^2)(val) < 0$ by Eq. (70) in agreement with the numerical value of $A_2^0(r^2)$ shown in TABLE 1. As shown by Eq. (70) the main contribution of the MA constant $k_1(T)$ is given by a product of $A_2^0$ and the positive value of Stevens factor $\Theta_5^{(0)}$, and $k_1(T)$ becomes positive. This means that the $K_1(T) > 0$ because $K_1^{TM}(T) > 0$.

On the other hand, second neighbor Fe(8j) and third neighbor Fe(8f) atoms of Sm atom are situated obliquely upward as shown in Fig. 5(b). According to the negative sign of $\Theta_{5d}^{(0)}(\theta, \varphi)$ shown in Fig. 5(d), we obtained $\Delta n_{5d}^{(4)} = -0.0013$ using Eq. (71), and $A_4^0(r^4)(val) < 0$ from Eq. (71).

Again the negative value is consistent with the numerical values of $A_4^0(r^4)$. The main contribution of MA constant $K_2(T)$ comes from a product of $A_4^0(r^4)$ and the positive value of $\Theta_5^{(0)}$, and results in $K_2(T) < 0$.

Thus, the sign of MA constants $K_1(T)$ and $K_2(T)$ are determined by the configuration of Sm and Fe atoms in the lattice. In the following, we investigate the J-mixing effect on single Sm magnetic properties at $T = 0$ K.

B. J-Mixing Effect and Zero-Temperature Magnetic Properties of SmFe_{12} Compound

To clarify the J-mixing effect on single-ion magnetic properties, we show the calculated results of the magnetic moments $m_{L,S}(0)$ and the MA constants $k_{1,2}(0)$ for model A, B, and C in TABLE 1. We used Eqs. (53) and (54) for $m_{L,S}(0)$ and Eqs. (56) and (57) for $k_{1,2}(0)$, and the values of $A_{n'}^{m}(r')$, $B_{ex}(0)$, and $M_{TM}(0)$ in TABLE 2. As a reference, we also show the results obtained by the statistical method: $m_{L,S}(0)$ in Eqs. (23) and (24) and $k_{1,2}(0)$ defined in Eqs. (19) and (20). Both the analytical and statistical results give $k_1(0) > 0$ and $k_2(0) < 0$, respectively.
Statistics

\[ 400 \]

exp 1: Sucksmith-Thompson

\[ 600 \]

500

\[ 300 \]

200

\[ 100 \]

model B is modified by the present model C in the whole MA constants of both magnetic moment in Fig. 6(a) and (b), respectively. The results show that magnetic moment in model C (present model) agree best with the statistical ones. Results in model C (present model) agree best with the statistical ones except for \( k_1 \).

TABLE III. Magnetic moments \( m_{L,S}(0) [\mu_B] \) in Eqs. (53) and (54) and MA constants \( k_{1,2}(0) [K] \) in Eqs. (56) and (57) for model A, B, and C at 0 K for single Sm ion. Results obtained by Boltzmann statistics of \( m_{L,S}(0,0) \) defined by Eqs. (23) and (24) and MA constants \( k_{1,2}(0) \) defined by Eqs. (19) and (20) are also shown in the fifth column.

| model | A | B | C | statistics |
|-------|---|---|---|------------|
| \( m_L \) | 4.29 | 5.04 | 4.62 | 4.70 |
| \( m_S \) | -3.57 | -5.08 | -4.24 | -4.39 |
| \( k_1 \) | 60.2 | 144.5 | 97.7 | 101.1 |
| \( k_2 \) | -14.0 | -74.6 | -40.9 | -23.5 |

\( k_2(0) < 0 \) for three models A, B, and C. The calculated results in model C (present model) agree best with the statistical ones.

We find that the absolute values of \( m_{L,S}(0) \) and \( k_{1,2}(0) \) in model B and C are larger than those in model A, which is attributed to inclusion of the \( J \)-mixing effects. The model B proposed in the previous studies overestimated the \( J \)-mixing effects by \( 1/R_J \) compared with model C, where \( R_J = 0.44 \) in Eq. (58) for SmFe\(_{12}\) compound. Actually, values of \( m_{L,S}^c \) and \( k_{1,2}^c \) in TABLE III satisfy the relation in Eq. (59) and (60). The results in present study (\( X=C \)) quantitatively agree well with statistical ones except for \( k_2^c(0) \). The discrepancy in \( k_2^c(0) \) may be due to omitting the 2nd order terms of \( A_2^0(r^2) \) in Eq. (57), which have a positive contribution independent of the sign of \( A_2^0(r^2) \).

C. Finite Temperature Magnetic Properties of SmFe\(_{12}\) Compound

Calculated results of finite temperature magnetic properties for a single Sm ion in equilibrium at \( e_B^T = n_B \) are shown in Fig. 6(a) and (b), respectively. The results show that the \( J \)-mixing effect in model B increases the absolute values of both \( m_{L,S}(T) \) and \( k_{1,2}(T) \). The over-estimation in model B is modified by the present model C in the whole

FIG. 5. (color online) (a) Atomic position of first (8i), second (8j), and third (8f) neighbor Fe atoms of Sm ion in SmFe\(_{12}\), (b) illustration of valence mechanism in SmFe\(_{12}\), and (c) typical tesseral harmonic functions as basis of CF Hamiltonian, where signs represent the phase.

FIG. 6. (color online) Temperature dependence of (a) magnetic moments of Sm ion \( m_{L,S}(T) \) and \( m(T) \) at \( B = 0 \) and (b) MA constants per single Sm ion \( k_{1,2}(T) \) calculated by using models A, B and C. Results obtained by Boltzmann statistics are shown by broken curves. (c) Temperature dependent MA constants \( K_{1,2}(T) \) in SmFe\(_{12}\) compound by using statistical method for Sm sublattice contribution \( k_{1,2}(T) \), which are compared with experimental ones by the Sucksmith-Thompson (circles) and the anomalous Hall effect (triangles). For both calculated and experimental results in Fig. 6(c), \( K_1(T) \) and \( K_2(T) \) are shown by solid and broken curves, respectively.
temperature range. Obtained results of model C reproduce well the statistical results for \( m_{L,S}(T,0) \) in Eqs. \( 29 \) and \( 30 \) and for \( k_{1,2}(T) \) in Eqs. \( 19 \) and \( 20 \) as shown by broken lines in Fig. \( 6 \)a) and (b).

The physical meaning of the increment of the absolute value of \( m_{L,S}(T) \) and \( k_{1,2}(T) \) by \( J \)-mixing may be given as follows. The expression of the free energy given by Eq. \( 43 \) includes the \( J \)-mixing effect in the second term of the square bracket. The term decrease \( f_{\text{ex}}(x) \) by \(-\mu_B B_{\text{ex}}(T)\delta S(T)\), where \( \delta S(T) = \frac{2(L+1)}{3(J+1)}T_j^0(T) > 0 \).

Because of the decrease in \( f_{\text{ex}}(x) \), the absolute value of the spin \( \langle C_0^{(l)}(\hat{S}) \rangle_0 \) and orbital moments \( \langle C_0^{(l)}(\hat{L}) \rangle_0 \) along \( e_0^{TM} \) are increased by \( \delta S(T) \). The tensor operators \( \langle C_0^{(l)}(\hat{L}) \rangle_0 \) for even \( l \) are also increased by \( \frac{l(l+1)}{2l+1}T_j^0(x) \), which contribute to increase in the absolute value of the MA constants \( k_p^{(q)}(T) \).

The magnetic moment of Sm ion \( m(T) \) is reversed at around \( T_{\text{comp}} = 350 \text{ K} \) in model C and calculation by Boltzmann statistics. The temperature is called compensation temperature. This phenomenon is observed also in other Sm compounds. Zhao et al pointed out that this phenomenon also appears at \( T = 337 \text{ K} \) in \( \text{Sm}_2\text{Fe}_7\text{N}_2 \) using statistical method including similar parameter values with ours such as \( \mu_B B_{\text{ex}}(0)/k_B = 300 \text{ K} \) and \( \lambda/k_B = 411 \text{ K} \). Their results are comparable with ours, however, the mechanism has not been surveyed. In the present model C, the magnetic moment of Sm ion can be written as \( m(T) = g_J \mu_B J B_j^1(x) - \mu_B \delta S(T) \). Because \( \mu_B \delta S(T) \) is proportional to \( T_j^1(x) \) and monotonically increasing with temperature below \( T/T_C = 0.8 \) as shown in Fig. \( 4 \)a), the term compensates the \( g_J \mu_B J B_j^1(x) \) at \( T_{\text{comp}} \).

Fig. \( 4 \)c) shows the results of \( K_1(T) \) and \( K_2(T) \) obtained by statistical method in \( \text{SmFe}_{12} \) compound, which are compared with experimental ones denoted by exp 1 and exp 2 measured by the Sucksmith-Thompson method and anomalous Hall effect, respectively. At the whole temperature region the results of \( K_1(T) \) agree well with the experiments. Our statistical results qualitatively reproduce the experimental results below 200 K. The negative \( K_2(T) \) at low temperatures is origin of first-order magnetization process (FOMP) as discussed below.

### D. Thermodynamic Properties of SmFe\(_{12}\) Compound

Fig. \( 7 \) shows calculated results of the Helmholtz free energy density \( F(e^{TM},T) \) given in Eq. \( 62 \) for model C as a function of \( e^{TM} \cdot n_a \) with \( e^{TM} \cdot n_b = 0 \) at \( T = 0 \text{ K} \) and \( 400 \text{ K} \), where \( n_{a(b)} \) is unit vector parallel to \( a(b) \)-axis. The results are compared with statistical ones of \( G(e^{TM},T,0) \) in Eq. \( 13 \). When the direction of \( e^{TM} \) is changed, the free energy density on both Sm and Fe sublattice are increased. For the Sm sublattice, the energy increase originates from the CF, which can be expressed by the \( \sum_j f_{\text{CF},j}(e^{TM},T) \) in Eq. \( 55 \), and for Fe sublattice, the energy increase can be written by: \( K_1^{TM}(T) \sin^2 \theta^{TM} \) with \( K_1^{TM}(T) = 1.966 \) and 0.387 MJ/m\(^3\) at 0 and 400 K, respectively, which are much smaller than those of Sm sublattice \( \sum_j k_{1,j}(T)/V_0 = 8.059 \) and 2.310 MJ/m\(^3\). The analytical results agree well with statistical ones.

Fig. \( 8 \) shows calculated results of magnetization curves in the equilibrium states of \( \text{SmFe}_{12} \) at \( T = 0 \) and \( 400 \text{ K} \), where the magnetic field \( B \) is applied along \( a \)-axis. Analytical results of the magnetization along the \( a \)-axis are compared with statistical ones. We have confirmed that the results in model C well reproduce the statistical ones. At \( T = 0 \), we find characteristic behavior of an abrupt change in the magnetization \( M_a(T) \cdot n_a \) at \( B = B_{\text{FP}} \). The change is called first-order magnetization process (FOMP) and the \( B_{\text{FP}} \) is called as FOMP field. At \( T = 400 \text{ K} \), no FOMP appears in both analytical and statistical results and the magnetization saturates at the MA field \( B_A \). In \( \text{SmFe}_{12} \), the magnetization curve at low temperatures were not reported, however, in \( \text{SmFe}_{11}\text{Ti} \) compound, FOMP observed at \( T = 5 \text{ K} \) and \( B_{\text{FP}} = 10 \text{ T} \), which is qualitatively consistent with our results.

Let us consider the magnetization process along \( c \)-axis and estimate nucleation field \( B_N \) in the model C. The magnetization is first saturated as \( M_a(T) \cdot n_c \) along \( c \)-axis by an infinitesimal field. Then the direction of the magnetic field is reversed and the magnitude is increased as \(-B n_c \). The original state continues to exist as a quasi-
FIG. 8. (color online) Magnetization curves of SmFe\(_{12}\) at \(T = 0\) and 400 K with applied field \(B\) parallel to \(a\)-axis in the equilibrium calculated by analytical (solid curves) and statistical (broken curves) methods in Eqs. (63) and (25), respectively, where \(\mu_0\) is the magnetic constant. Dashed-dotted lines show tangent lines of magnetization curves at \(B = 0\): \(y = (\mu_0 M_s(T))^2/2K_1B\). Values of \(B\) at the circles correspond to the nucleation field \(B_N(T)\) obtained by using the free energy density of model C (see text).

where we use the approximate free energy density: \(F(e^{TM}, T) = K_1(T) \sin^2 \theta^{TM} + K_2(T) \sin^4 \theta^{TM}\), in which the small contributions \(K_3(T), K_4(T)\) are neglected. Details are shown in Appendix A. Calculated results of \(B_N(T), B_{FP}(T)\), and \(B\_A(T)\) are shown in Fig. 9. The condition of FOMP appearance in model C is given by \(-K_2(T) < K_1(T) < -6K_2(T)\) between \(0 < x_{FP}(T) < 1\) in Eq. (74). As for SmFe\(_{12}\) compound, the FOMP is realized below \(T = 281\) K \(\equiv T_{FP}\), which is analytically obtained from the condition: \(K_1(T) = -6K_2(T)\). The curves of \(B_{FP}(T)\) and \(B\_A(T)\) are continuously connected at \(T_{FP}\), which is called as FOMP temperature. When \(K_1(T) < -2K_2(T)\) the magnetization direction is in-plane at \(B = 0\).

V. SUMMARY

The temperature dependence of magnetic anisotropy (MA) constants and magnetization of SmFe\(_{12}\) were investigated by using two methods for the model Hamiltonian which combines quantum and phenomenological ones for rare-earth (\(R\)) and Fe subsystems, respectively. Parameter values of \(R\) Hamiltonian were determined by the first-principles. First method adopts a numerical procedure with Boltzmann statistics for the Sm 4f electrons. The other one is an analytical method which deals with the magnetic states of \(R\) ions with strong mixing of states with different quantum number of angular momentum \(J\) (\(J\)-mixing). We have modified the previous analytical
methods for Sm ions which have relatively small spin-orbit interaction, and clarified that they over-estimate the J-mixing effects for Sm-transition metal compounds. It has been shown that the results of our analytical method agree with those obtained by statistical method. Our analytical method revealed that the increasing spin angular momentum with J-mixing caused by strong exchange field, enhances the absolute value of orbital angular momentum and MA constants via spin-orbit interaction, and that these J-mixing effects remain even above room temperature. The calculated results of MA constants show that $K_1(T) > 0$ and $K_2(T) < 0$ in SmFe$_{12}$ in consistent with experiment.

The peculiar temperature dependence known as first-order magnetization process (FOMP) in SmFe$_{12}$ has been attributed to the negative $K_2$. It was also verified that the requirement for the appearance of FOMP is given as $-6K_2 < K_1 < -2K_2$. The positive (negative) $K_{1(2)}$ appears due to an increase in the crystal field parameter $A_0^0(r^2)$ ($A_0^4(r^4)$) caused by hybridization between 3d-electrons of Fe on 8i (8j) site and 5d and 6п valence electrons on Sm. The mechanism of $K_{1(2)}$ in SmFe$_{12}$ has been thus clarified by using the expressions of $K_1$ and $K_2$ obtained in the analytical method. Shortly, the sign of $K_1$ and $K_2$ in SmFe$_{12}$ is attributed to the characteristic lattice structure around Sm ions, that is, crystallographic $2b$-sites on $c$-axis adjacent to Sm are vacant. We also present results on the magnetization process and nucleation fields by calculating Gibbs free energy.

The present method will be applied to derive a general expression of the free energy to analyze MA of non-uniform systems such as disordered compounds, surfaces, and interfaces. The results will be reported in a forthcoming paper.

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**Appendix A: Magnetization Process in Condition of $K_1(T) > 0$ and $K_2(T) < 0$**

To investigate the magnetization process in equilibrium along the $c$-plane (e.g. $a$-axis), we introduce the simplified model with magnetic anisotropy constants $K_1(T) > 0$ and $K_2(T) < 0$, which can be expressed by the Gibbs free energy as:

$$G(x, T, B) = K_1(T)x^2 + K_2(T)x^4 - BM_s(T)x$$

(A1)

where $x = M_s(T) \cdot n_a / M_s$ with total magnetization $M_s$ and unit vector parallel to $a$-axis $n_a$. $T$ and $B = Bn_s (B > 0)$ are temperature and applied magnetic field, respectively. The equilibrium condition is:

$$G(x_0, T, B) = \min_{|x| \leq 1} G(x, T, B),$$

where $x = x_0(T, B)$ gives minimum of $G(x, T, B)$. For $K_1(T) \leq -K_2(T)$, the magnetization is always tilted to the $a$-axis direction due to $x_0(T, B) = 1$. Otherwise, the magnetization curve is given by:

$$M_s(T, B) \cdot n_a = M_s(T)x_0(T, B).$$

(A2)

The first-order magnetization process (FOMP) appears, when $x_0(T, B)$ has two values at certain $B$, which is called as FOMP field $B_{FP}$.

To determine the $x_0(T, B)$ for $K_1(T) > -K_2(T)$, we show the first and second derivative of $G(x, T, B)$ with respect to $x$ as:

$$\frac{\partial G(x, T, B)}{\partial x} = 2K_1(T)x + 4K_2(T)x^3 - BM_s(T),$$

(A3)

$$\frac{\partial^2 G(x, T, B)}{\partial x^2} = 2K_1(T) + 12K_2(T)x^2.$$  

(A4)

A inflection point of $G(x, T, B)$ for $x > 0$ at fixed $T$ and $B$ is given by $x_c(T) = \sqrt{-K_1(T)/6K_2(T)}$. Hereafter, we consider following two cases: $x_c(T) \geq 1$ and $x_c(T) < 1$.

(i) The case of $x_c(T) \geq 1$.

$x_0(T, B)$ is obtained from the condition $\partial G(x, T, B)/\partial x = 0$ for $0 < x \leq 1$, because $\partial^2 G(x, T, B)/\partial x^2 > 0$ is always satisfied. The saturating point of magnetization $x_0(T, B) = 1$ is obtained from the condition $\partial G(x, T, B)/\partial x|_{x=1} = 0$ as:

$$B = \frac{2K_1(T)}{M_s(T)}[1 + 2\gamma(T)] \equiv B_A(T),$$

(A5)

where $\gamma(T) = K_2(T)/K_1(T)$. The $B_A$ is so-called anisotropy field.

(ii) The case of $x_c(T) < 1$.

$x_0(T, B)$ is obtained from the condition $G(x_0(T, B), T, B)$ where $x_c(T, B)$ is determined by the condition of local minimum as: $\partial G(x_c(T, B), T, B)/\partial x = 0$ and $x_c(T, B) < x_c(T)$. In the magnetization process, $x_0(T, B)$ is continuously increased from zero with increasing $B$ according to $x_0(T, B) = x_c(T, B)$ for $G(x_c(T, B), T, B) < G(1, T, B)$. At $B = B_{FP}$ such that $G(x_c(T, B), T) = G(1, T, B)$ is satisfied, $x_0(T, B)$ shows the abrupt jump and becomes saturated value of $x_c(T, B) = 1$. The condition is rewritten as:

$$[x_0 - 1] \left[3K_2(T)x_0^3 + 2K_2x_0 + K_1(T) + K_2(T)\right] = 0.$$  

(A7)
By solving the Eq. \((A7)\) for \(0 < x_0 \leq 1\), two minimum points of \(G(x, T, B)\) with respect to \(x\) are obtained at \(x_0(T, B) = 1\) and

\[
x_0(T, B) = \frac{1}{3} \left( -1 + \sqrt{-\frac{3}{\gamma(T)} - 2} \right) ≡ x_{FP}(T). \quad (A8)
\]

By using \(x_{FP}(T)\), the field at which the FOMP occurs is determined by:

\[
B = \frac{2K_1(T)}{M_s(T)} [x_{FP}(T) + 2\gamma(T)x_{FP}(T)^3] ≡ B_{FP}(T). \quad (A9)
\]

As a result, for \(-1 < \gamma(T) < -1/6\), the FOMP occurs between \(M_s(T) \cdot n_\alpha = M_s(T)x_{FP}(T)\) and \(M_s(T)\).

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