

Magnetocrystalline anisotropy of 3d-4f intermetallics: Breakdown of the linear theory

M. D. Kuz'min* and J. M. D. Coey

Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland

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Applicability of linear theory to magnetic anisotropy of 3d-4f intermetallics is investigated with particular reference to $\text{Sm}_2\text{Fe}_{17}\text{N}_3$. A general quantitative criterion for the breakdown of the linear theory is established, according to which the theory falls beyond a 20% accuracy limit for most permanent magnet materials. By rigorous numerical treatment of published experimental data on high-field magnetization of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, the crystal-field parameters are determined to be $A_2^0 = -333\text{Ka}_0^{-2}$, $A_4^0 = 0.84\text{Ka}_0^{-4}$. The linear theory fails for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ due to its disregard for both J -mixing, predominant at all temperatures, and the intramultiplet nonlinear effects, important at low temperatures. Nevertheless these effects can be largely compensated for by rescaling the crystal-field parameters within the framework of the linear theory, which then provides an accurate analytical description of anisotropic magnetic properties of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ in the practically important range of temperatures, $T \gtrsim 300\text{ K}$.

I. INTRODUCTION

Magnetic anisotropy of 3d-4f intermetallics is known to originate mainly from the crystal field (CF) acting on the unfilled 4f shell of the rare earths. Broadly speaking, there are two approaches to calculating the magnetic anisotropy; linear theory and numerical calculations based on the complete Hamiltonian. Series expansion methods may be useful at high temperatures.¹ The justification for continuing to make approximations rather than looking for exact numerical solutions is the convenience of analytical expressions for calculations and the physical insight into the parameters that they provide. The temperature dependence of the rare-earth contribution to the anisotropy energy can be described analytically on the basis of a linear approximation which takes account of corrections to first order in the crystal field, thus regarded as a weak perturbation with respect to the stronger 3d-4f exchange interaction. Within this framework, some particular cases that have been investigated include the low-temperature limit, for which Zener's $n(n+1)/2$ power law was established² where $n=2,4,6$ is the order of the CF interaction. Expressions relating the anisotropy constants K_i to the CF parameters A_n^m have been obtained for $T=0$.³ These low-temperature expressions find application in the theory of spin waves⁴ and hyperfine interactions.⁵ Another important particular case within the same linear approximation is the $J=\infty$ classical limit where expressions for the temperature dependence of the anisotropy constants at arbitrary T were obtained by Keffer⁶ and further discussed by Callen and Callen.⁷ A recent review of the application of linear theory of magnetocrystalline anisotropy to the well-known $\text{R}_2\text{Fe}_{14}\text{B}$ intermetallic compounds has been given by Herbst.⁸

Recently a general analytical solution for arbitrary J has been described⁹ in terms of the CF parameters and generalized Brillouin functions, $B_J^n(x)$. For a uniaxial crystal the corresponding expressions are (note the

difference in notation between Ref. 9 which uses the Wybourne normalization for the CF parameters and the present work which uses the Stevens normalization^{5,10}) (in $K/\text{rare earth}$):

$$E_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta, \quad (1)$$

where

$$K_1 = -3\alpha_J J^2 A_2^0 \langle r^2 \rangle B_J^2(x) - 40\beta_J J^4 A_4^0 \langle r^4 \rangle B_J^4(x) - 168\gamma_J J^6 A_6^0 \langle r^6 \rangle B_J^6(x), \quad (2a)$$

$$K_2 = 35\beta_J J^4 A_4^0 \langle r^4 \rangle B_J^4(x) + 378\gamma_J J^6 A_6^0 \langle r^6 \rangle B_J^6(x), \quad (2b)$$

$$K_3 = -231\gamma_J J^6 A_6^0 \langle r^6 \rangle B_J^6(x), \quad (2c)$$

and the magnetothermal ratio

$$x = 2J|g_J - 1|\mu_B B_{\text{ex}}/kT. \quad (3)$$

Here B_{ex} is the exchange field acting on the rare-earth sublattice.

Expressions (2) describe the temperature dependence of the anisotropy constants by means of the generalized Brillouin functions $B_J^n(x)$, which are tabulated in Ref. 9. The constants in the expressions are the uniaxial CF parameters A_n^0 and the Stevens coefficients α_J , β_J , γ_J .¹¹ The expressions take no account of J -mixing effects.

The main concern about applicability of Eqs. (1)–(3) to real intermetallic compounds arises because these equations are still based on a linear approximation where $A_n^0 \langle r^n \rangle / \mu_B B_{\text{ex}}$ are regarded as small parameters. A typical value of B_{ex} in rare-earth-iron or rare-earth-cobalt compounds is $\sim 400\text{ T}$, whereas the leading CF parameter A_2^0 in the best permanent magnet materials can amount to $\sim 300\text{Ka}_0^{-2}$, which yields $A_2^0 \langle r^2 \rangle / \mu_B B_{\text{ex}} \sim 1$. This casts doubt on the applicability of the linear theory to the systems concerned and calls for a

more accurate quantitative criterion.

We first establish such a criterion and show that most of the $3d-4f$ intermetallics used for permanent magnet applications fall beyond the limits of the linear theory (deviations of more than 20%). We then investigate the consequences of the breakdown of the linear theory of magnetic anisotropy with particular reference to the novel permanent magnet material $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, considering both intramultiplet nonlinear effects and J mixing.

II. CRITERION FOR THE BREAKDOWN OF THE LINEAR THEORY

In this section we examine effects quadratic in the CF, which chiefly contribute to the breakdown of the linear theory, and establish the quantitative criterion for breakdown. We postpone consideration of J -mixing effects and restrict ourselves to the leading term in the CF interaction. Thus, we proceed from the following rare-earth Hamiltonian:

$$\hat{H}_R = 2(g_J - 1)\mu_B \mathbf{B}_{\text{ex}} \hat{\mathbf{J}} + \alpha_J A_2^0 \langle r^2 \rangle O_2^0(\hat{\mathbf{J}}'), \quad (4)$$

where the first term describes the $3d-4f$ exchange interaction as the effect of an exchange field $\mathbf{B}_{\text{ex}} = -n_{fd}\mathbf{M}_d$ originating from the ferromagnetically ordered $3d$ subsystem. This field acts only on the rare-earth spin $\hat{\mathbf{S}}$ [cf. Eq. (17)

below], the factor $g_J - 1$ appears after projecting this operator onto the ground J manifold of the rare earth. The second term in Eq. (4) is the leading CF term, regarded as a perturbation with respect to the exchange. We shall also restrict ourselves to the case of zero temperature, when according to Sec. IV C the intramultiplet nonlinear effects are most pronounced. This necessitates taking into account anisotropic corrections only to the ground-state energy of the rare earth. The unperturbed ground state is $|J, M_J\rangle$, $M_J = J$, with the quantization axis z being defined by $\mathbf{B}_{\text{ex}}$, or the $3d$ magnetization $\mathbf{M}_d$.

Since the perturbation $\alpha_J A_2^0 \langle r^2 \rangle O_2^0(\hat{\mathbf{J}}')$ is referred to the crystallographic (primed) coordinate system, it has to be transformed into the exchange-field-related (nonprimed) coordinates, where the z axis is parallel to $\mathbf{B}_{\text{ex}}$ and the y axis lies in the basal plane. This transformation is¹²

$$O_2^0(\hat{\mathbf{J}}') = \frac{1}{2}(3 \cos^2 \theta - 1)O_2^0(\hat{\mathbf{J}}) - 3 \sin 2\theta O_2^1(\hat{\mathbf{J}}) + \frac{3}{2} \sin^2 \theta O_2^2(\hat{\mathbf{J}}). \quad (5)$$

Here $O_2^0(\hat{\mathbf{J}}) \equiv 3\hat{J}_z^2 - J(J+1)$, $O_2^1(\hat{\mathbf{J}}) \equiv \frac{1}{2}(\hat{J}_x \hat{J}_z + \hat{J}_z \hat{J}_x)$, and $O_2^2(\hat{\mathbf{J}}) \equiv \hat{J}_x^2 - \hat{J}_y^2$ are the conventional Stevens operators.¹¹ To second order in perturbation theory, the ground-state energy is

$$E_0 = -J\Delta_{\text{ex}} + \frac{1}{2}(3 \cos^2 \theta - 1)\alpha_J A_2^0 \langle r^2 \rangle \langle J, J | O_2^0 | J, J \rangle - 36 \sin^2 \theta \cos^2 \theta (\alpha_J A_2^0 \langle r^2 \rangle)^2 \Delta_{\text{ex}}^{-1} | \langle J, J | O_2^1 | J, J-1 \rangle |^2 - \frac{9}{8} \sin^4 \theta (\alpha_J A_2^0 \langle r^2 \rangle)^2 \Delta_{\text{ex}}^{-1} | \langle J, J | O_2^2 | J, J-2 \rangle |^2, \quad (6)$$

where $\Delta_{\text{ex}} \equiv 2|g_J - 1|\mu_B B_{\text{ex}}$ is the exchange splitting. Calculating the matrix elements in Eq. (6) and omitting terms independent of θ , we write the anisotropic part of E_0 in form (1) where

$$K_1 = -\frac{3}{2}\alpha_J A_2^0 \langle r^2 \rangle J(2J-1) - \frac{9}{2}\Delta_{\text{ex}}^{-1}(\alpha_J A_2^0 \langle r^2 \rangle)^2 J(2J-1)^2, \quad (7)$$

$$K_2 = \frac{9}{8}\Delta_{\text{ex}}^{-1}(\alpha_J A_2^0 \langle r^2 \rangle)^2 J(2J-1)(8J-5), \quad (8)$$

$$K_3 = 0. \quad (9)$$

The first term of Eq. (7) appeared in the first approximation; cf. (7) and (2a) when $A_4^0 = A_6^0 = 0$ and $T = 0$, i.e., $x = \infty$; note that $J(2J-1) = 2J^2 B_J^2(\infty)$.⁹ The second-order corrections, as one can see from Eqs. (7)–(9), not only rescale K_1 but also result in a nonzero K_2 , although no allowance has been made for fourth-order CF terms. This quadratic in the A_2^0 contribution to K_2 may well outweigh the linear one, $\propto A_4^0, A_6^0$, see (2b). This is the case for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, where the linear theory (Sec. IV B) predicts $K_2 = \frac{65}{99} A_4^0 \langle r^4 \rangle = 1.25$ K, whereas according to (8) it should be 222 K.

The quantity of primary interest is the anisotropy field, which in the easy-axis case is given by

$$B_a = M_s^{-1}(2K_1 + 4K_2), \quad (10)$$

where M_s is the spontaneous magnetization. [The anisotropy field defined by Eq. (10) has the meaning of the saturation field of the transverse magnetization (see Sec. IV B below) and can be deduced from high-field magnetization data on well-oriented samples. It should be distinguished from the quantity $B'_a = 2K_1/M_s$ which is also commonly called the anisotropy field but has a distinct meaning—nucleation field for coercivity in isolated single-domain particles and can be deduced from magnetization data in low fields.] Before substitution into Eq. (10), Eqs. (7)–(9) should be multiplied by $N_R k$, where N_R is the number of rare earth atoms per cubic meter, for conversion from $K/\text{rare earth}$ to J/m^3 . Thus we get

$$B_a = B_a^{\text{linear}}(1 + \epsilon), \quad (11)$$

where

$$B_a^{\text{linear}} = -3N_R k M_s^{-1} \alpha_J A_2^0 \langle r^2 \rangle J(2J-1) \quad (12)$$

and

$$\epsilon = -G \frac{A_2^0 \langle r^2 \rangle}{\mu_B B_{\text{ex}}}, \quad (13)$$

where $G = (3/4)\alpha_J(4J-3)/|g_J-1|$. According to Eq. (11), in order for the linear approximation to be valid, ϵ must be small compared with unity. Therefore, this quantity can be chosen as a quantitative measure of the

TABLE I. Combination of ionic constants G of Eq. (13) for tripositive rare earths, given as both vulgar and decimal fractions.

Ce	$-\frac{21}{10}$	-2.100
Pr	$-\frac{169}{165}$	-1.024
Nd	$-\frac{35}{132}$	-0.265
Sm	$\frac{91}{300}$	0.303
Tb	$-\frac{7}{22}$	-0.318
Dy	$-\frac{27}{70}$	-0.386
Ho	$-\frac{29}{150}$	-0.193
Er	$\frac{9}{35}$	0.257
Tm	$\frac{21}{22}$	0.955
Yb	$\frac{11}{6}$	1.833

accuracy of the linear theory. In the case of easy-axis magnets it provides a direct estimate for the fractional error in the rare earth contribution to the anisotropy field at zero temperature. Apart from the familiar ratio $A_2^0 \langle r^2 \rangle / \mu_B B_{\text{ex}}$, ϵ contains a combination of ionic constants G tabulated in Table I. According to these data, the linear approximation holds better for the middle of the rare-earth series than at either end. Numerical values of ϵ for some uniaxial intermetallics are given in Table II.

It can be seen from Table II that, whereas some intermetallics may be reasonably well described by the linear theory, the important permanent magnet materials fall beyond the 20% limit and thus require further attention. No general analytical investigation can then be carried out, so numerical methods will be used.

III. RIGOROUS DESCRIPTION OF ANISOTROPIC MAGNETIC PROPERTIES OF $\text{Sm}_2\text{Fe}_{17}\text{N}_3$

A. The model

We now formulate the model,¹³ hereafter referred to as model 1, used for numerical investigation of both J mixing and nonlinear CF effects. The total free energy,

$$F = F_{\text{Fe}} - N_R kT \ln \{ \text{tr} [\exp(-\hat{H}_R / kT)] \} , \quad (14)$$

consists of two parts, the first of which,

TABLE II. The leading CF parameters, A_2^0 , 3d-4f exchange fields, B_{ex} , and the second-order corrections for the anisotropy fields at $T=0$, ϵ , for some permanent magnet materials.

Compound	A_2^0 (Ka_0^{-2})	B_{ex} (T)	ϵ (%)	Reference
SmCo_5	-200	260	34	28
$\text{Nd}_2\text{Fe}_{14}\text{B}$	295	520	25	24
$\text{Sm}_2\text{Fe}_{17}$	> -36	450	< 4	29
$\text{Sm}_2\text{Fe}_{17}\text{N}_3$	-333	320	46	This work
$\text{Sm}_2\text{Fe}_{17}\text{C}_3$	-180	320	25	29
$\text{NdFe}_{11}\text{TiN}$	~400	~350	50	Estimated
$\text{SmFe}_{11}\text{Ti}$	-132	353	16	30

$$F_{\text{Fe}} = K_{\text{Fe}}(T) \sin^2 \theta - \mathbf{M}_{\text{Fe}}(T) \mathbf{B} , \quad (15)$$

describing the Fe subsystem's behavior, is assumed to be known from study of an isostructural compound with a nonmagnetic rare earth, $\mathbf{B}$ is an external magnetic field. In this work we use the following empirical formulas, obtained by fitting experimental data for Y_2Fe_{17} :^{14,15}

$$M_{\text{Fe}}(T) = M_{\text{Fe}}(0)(1.9\sqrt{\tau} - 0.9\tau) ,$$

$$K_{\text{Fe}}(T) = K_{\text{Fe}}(0)(0.81\tau + 1.38\tau^2 - 1.19\tau^3) , \quad (16)$$

$$\tau = 1 - T/T_C ,$$

with the values $\mu_0 M_{\text{Fe}}(0) = 1.6$ T, $K_{\text{Fe}}(0) = -1.9$ MJ/m³ obtained for $\text{Y}_2\text{Fe}_{17}\text{N}_3$ (Ref. 16) and $T_C = 749$ K for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$.¹⁷ The second term of Eq. (14) originates from the single-ion rare-earth Hamiltonian.

$$\hat{H}_R = \lambda \hat{\mathbf{L}} \hat{\mathbf{S}} + 2\mu_B \mathbf{B}_{\text{ex}} \hat{\mathbf{S}} + \mu_B \mathbf{B} (2\hat{\mathbf{S}} + \hat{\mathbf{L}}) + \hat{H}_{\text{CF}} . \quad (17)$$

The rare-earth term is under investigation in this work. $\hat{H}_R$ includes terms describing the spin-orbit, R -Fe exchange, Zeeman, and CF interactions. The spin-orbit coupling constant λ is taken equal to 411 K, so as to account for the observed splitting, $\frac{7}{2}\lambda = 1440$ K,¹⁸ between the ground and the first excited multiplets of Sm^{3+} . No account is taken of the R - R exchange interaction. The R -Fe exchange is treated in the mean-field approximation, $\mathbf{B}_{\text{ex}} = -n_{R\text{Fe}} \mathbf{M}_{\text{Fe}}$. B_{ex} has been measured directly by inelastic neutron scattering in $\text{Gd}_2\text{Fe}_{17}\text{N}_3$, where a value of 199 ± 8 T is found.¹⁹ The value in $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ will certainly be greater since it has been established that $n_{R\text{Fe}}$ drops by about 30% from the light to the heavy rare earths.²⁰ We therefore take $n_{R\text{Fe}} = 200\mu_0$ for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, which is less than the value obtained from the Curie temperature.²¹

The local symmetry of the rare-earth site, $3m$, dictates the following form for the CF Hamiltonian:

$$\begin{aligned} \hat{H}_{\text{CF}} = & A_2^0 \sum_e (3z_e^2 - r_e^2) + A_4^0 \sum_e (35z_e^4 - 30z_e^2 r_e^2 + 3r_e^4) \\ & + A_4^3 \sum_e z_e (x_e^3 - 3x_e y_e^2) + \text{sixth-order terms} , \end{aligned} \quad (18)$$

but we shall retain only two leading terms (the sums are taken over all 4f electrons). The CF parameters A_2^0 and A_4^0 are regarded as adjustable parameters. In the case of Sm^{3+} , unless otherwise stated, we shall project $\hat{H}_R$ onto a set of states comprising the three lowest J manifolds ($J = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$), which proves to be sufficient to take full account for the J -mixing effects.²¹ The trace in Eq. (14) is taken after numerical diagonalization of the corresponding Hamiltonian matrix. Terms of the sixth order have no matrix elements within the ground multiplet $J = \frac{5}{2}$ and therefore have minor effect on magnetic anisotropy, due only to J mixing; the term containing A_4^3 is also unimportant (taking $A_4^3 = \pm 100 K a_0^4$ yields at the most a 3% reduction in anisotropy field at low temperatures; similar results were quoted by Kato *et al.*²³) since its major, linear contribution to the magnetic anisotropy vanishes for the $\text{Th}_2\text{Zn}_{17}$ -type structure.⁹ Thus, in this work $\hat{H}_{\text{CF}}$ has a uniaxial symmetry.

Because spin and orbital contributions to the magnetic moments of Sm^{3+} largely counterbalance each other, the net Sm magnetic moment is small,²² in this work it is simply neglected, $\mathbf{M}_s \equiv \mathbf{M}_{\text{Fe}}$.

B. Results

We carried out calculations of the reduced magnetization $\mathbf{m} \equiv \mathbf{M}_s / M_s \equiv \mathbf{M}_{\text{Fe}} / M_{\text{Fe}}$ as a function of applied magnetic field at various fixed temperatures. Because $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ is an easy-axis magnet at all temperatures below T_C , it was of interest to follow the behavior of the reduced transverse magnetization $m_\perp = \sin\theta$ versus the field applied at right angle to the c axis (Fig. 1). The problem thus reduced to finding the equilibrium angle θ by minimizing the total free energy (14).

The values of the CF parameters $A_2^0 = -333Ka_0^{-2}$ and $A_4^0 = 0.84Ka_0^{-4}$ were found to fit the experimental data on aligned powder of $\text{Sm}_2\text{Fe}_{17}\text{N}_{3.0}$.²³ In Fig. 2, the experimental data and results calculated using model 1 are shown by thick and thin solid lines, respectively.

One can notice that in small magnetic fields the experimental value of $m_\perp$ exceeds the calculated one, whereas in strong fields the calculated $m_\perp$ becomes larger. This is probably due to imperfect alignment of the powder. The misalignment can be simulated by assuming that the field is applied at an angle slightly less than 90° with respect to the c axis.²³

The calculated anisotropy field B_a , where $m_\perp$ reaches saturation, is plotted against temperature in Fig. 3(a) (solid curve). The anisotropy field B'_a , which is the field at which the initial slope of $m_\perp$ extrapolates to saturation, is much less temperature dependent [Fig. 3(b), solid curve]. It is more accessible to experimental measurement than B_a , especially at low temperatures where B_a exceeds the currently accessible experimental range.

Li and Coey²¹ using the same model as described in the previous subsection, with $\lambda = 411$ K and $n_{\text{RFe}} = 300\mu_0$, found a smaller value for A_2^0 , $-242Ka_0^{-2}$. The difference is mainly due to their choice of a larger value for n_{RFe} .

It should be also noted that the fit by Kato *et al.*²³ of their own data yielded unreasonably large values for the CF parameters, $A_2^0 = -600Ka_0^{-2}$, $A_4^0 = -20Ka_0^{-4}$, which led to reconsideration of their results in the present work. The choice of $n_{\text{RFe}} = 250\mu_0$ in Ref. 23 should have resulted in $A_2^0 \approx -300Ka_0^{-2}$, $A_4^0 \approx 0$ (Fig. 1 of Ref. 21 provides an illustration of this effect). However,

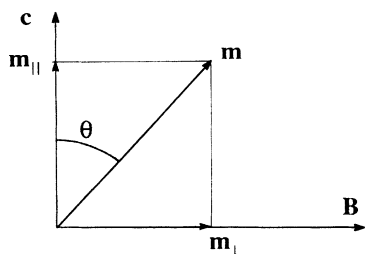


FIG. 1. Mutual orientation of the crystallographic c axis, applied magnetic field $\mathbf{B}$, and reduced magnetization vector $\mathbf{m}$.

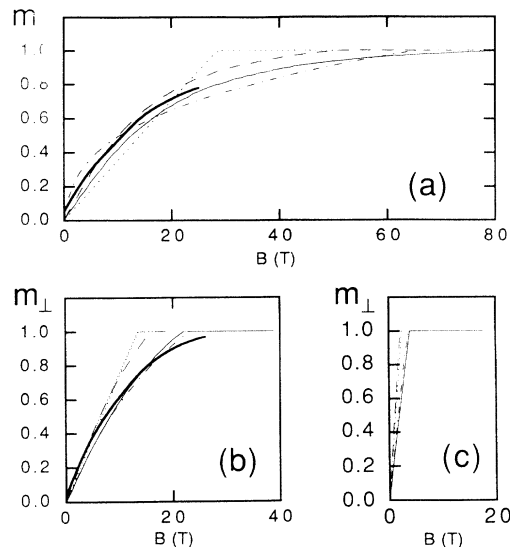


FIG. 2. Transverse reduced magnetization of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ vs magnetic field applied at the right angle to the c axis, as shown in Fig. 1: (a) $T = 4.2$ K, (b) $T = 296$ K, (c) $T = 673$ K. —, experimental data (Ref. 23); —, model 1; — — —, model 2; · · · · ·, model 3; - · - · -, model 4.

er, the J -mixing effect was exaggerated in Ref. 23 as well as in preceding work²⁴ by taking a smaller spin-orbit coupling constant, $\lambda = 350$ K, possibly obtained through the relation $\lambda = \zeta/5$ from the one-electron spin-orbit parameter $\zeta = 1730$ K;²⁵ however, that relation, based on the Russel-Saunders approximation, is inexact for heavy atoms such as rare earths.

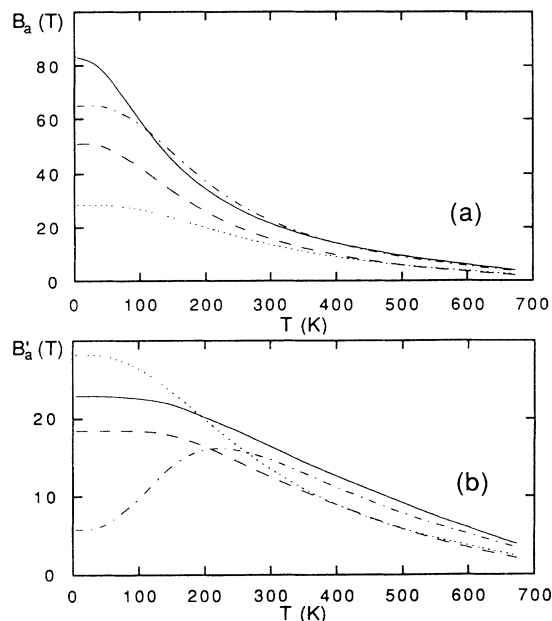


FIG. 3. Anisotropy field vs temperature for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$: (a) saturation field B_a , (b) nucleation field B'_a . —, model 1; — — —, model 2; · · · · ·, model 3; - · - · -, model 4.

IV. SIMPLIFIED DESCRIPTION OF $\text{Sm}_2\text{Fe}_{17}\text{N}_3$

In this section we abandon the above rigorous approach, as we gradually simplify the model, so the role of individual effects neglected at each step will become apparent. The models considered are as follows; model 1, rigorous with J mixing, numerical (Sec. III); model 2, rigorous but no J mixing, numerical (Sec. IV A); model 3, linear approximation, analytical (Sec. IV B); model 4, linear approximation with effective CF parameters, analytical (Sec. IV C).

A. No J mixing

We restrict ourselves to the ground multiplet $J = \frac{5}{2}$ of Sm^{3+} . The Hamiltonian (17) reduces to

$$\hat{H}_R = 2(g_J - 1)\mu_B \mathbf{B}_{\text{ex}} \hat{\mathbf{J}} + g_J \mu_B \mathbf{B} \hat{\mathbf{J}} + A_2^0 \alpha_J \langle r^2 \rangle O_2^0 + A_4^0 \beta_J \langle r^4 \rangle O_4^0. \quad (19)$$

We have omitted the spin-orbit term, which within the multiplet had reduced to a constant, -15λ . The Landé factor for the ground multiplet of Sm^{3+} is less than unity, $g_J = \frac{2}{7}$, meaning that the spin is antiparallel to the total moment.

No sixth-order CF terms enter the Hamiltonian (19) since the corresponding Stevens coefficient γ_J is zero for $J = \frac{5}{2}$. Although the crystal symmetry allows a nonzero CF term $A_4^3 \beta_J \langle r^4 \rangle O_4^3$, it was left out in (19), because its influence on the magnetic anisotropy is small (and vanishes in the linear approximation, see next subsection).

The calculation of $m_{\perp} = \sin\theta$ consists once again in minimizing with respect to θ the total free energy (14), where the trace is taken upon diagonalization of the 6×6 matrix of the Hamiltonian (19). This model is hereafter referred to as model 2. Having assumed the same values for the CF parameters, $A_2^0 = -333Ka_0^{-2}$ and $A_4^0 = 0.84Ka_0^{-4}$, we arrived at the $m_{\perp}(B)$ dependences shown in Fig. 2 with dashed lines. One can see that neglecting J mixing leads to considerable distortion of the $m_{\perp}(B)$ curves—at all temperatures $m_{\perp}$ in model 2 grows faster with magnetic field and reaches saturation at a smaller field value than in model 1. The corresponding anisotropy values are plotted against temperature in Fig. 3. The gaps between the solid and the dashed curves in Fig. 3 (models 1 and 2, respectively) persist over the whole range of temperatures.

B. Linear approximation

A further step in simplification of the model is to treat the last two terms in (19), i.e., the CF, as perturbation with respect to the first term, representing the Sm-Fe exchange interaction. The second, Zeeman term of (19) is neglected and consideration is limited to the first-order energy corrections, linear in the CF parameters. This step appears crucial for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, because it makes analytical calculation of $m_{\perp}(B)$, $B_a(T)$, and $B'_a(T)$ possible. The total free energy (14) now takes the following very simple form:

$$F = K_1 \sin^2\theta + K_2 \sin^4\theta - \mathbf{M}_{\text{Fe}} \mathbf{B}, \quad (20)$$

where the anisotropy constants are

$$\begin{aligned} K_1 &= K_{\text{Fe}}(T) - N_R k \left[\frac{65}{84} A_2^0 \langle r^2 \rangle B_{5/2}^2(x) \right. \\ &\quad \left. + \frac{8125}{2079} A_4^0 \langle r^4 \rangle B_{5/2}^4(x) \right], \\ K_2 &= \frac{8125}{2376} N_R k A_4^0 \langle r^4 \rangle B_{5/2}^4(x), \end{aligned} \quad (21)$$

the generalized Brillouin functions are

$$\begin{aligned} B_{5/2}^2(x) &= \frac{7}{5} + \frac{3}{25} \coth^2 \left[\frac{x}{5} \right] - \frac{18}{25} \coth \left[\frac{x}{5} \right] \coth \left[\frac{6}{5}x \right], \\ B_{5/2}^4(x) &= \frac{189}{125} + \frac{306}{125} \coth^2 \left[\frac{x}{5} \right] + \frac{21}{125} \coth^4 \left[\frac{x}{5} \right] \\ &\quad - \left[\frac{126}{125} \coth \left[\frac{x}{5} \right] + \coth \left[\frac{6}{5}x \right] \right], \end{aligned} \quad (22)$$

and the magnetothermal ratio is given by

$$x = \frac{25}{7} \frac{\mu_B n_{\text{RFe}} M_{\text{Fe}}(T)}{kT}. \quad (23)$$

The above result follows directly from Eqs. (2).⁹

When $\mathbf{B} \parallel c$, $K_1 > 0$, and $K_2 > 0$, which is the case, minimization of (20) with respect to $m_{\perp} \equiv \sin\theta$ yields²⁶

$$m_{\perp} = \left[\frac{2K_1}{3K_2} \right]^{1/2} \sinh \left\{ \frac{1}{3} \sinh^{-1} \left[\frac{3M_{\text{Fe}} B}{2K_1} \left[\frac{3K_2}{2K_1} \right]^{1/2} \right] \right\}. \quad (24)$$

Equation (24) is valid when $B < B_a$,

$$\begin{aligned} B_a &= \frac{2K_1 + 4K_2}{M_s} \\ &= \frac{2}{M_s} \left\{ K_{\text{Fe}}(T) - N_R k \left[\frac{65}{84} A_2^0 \langle r^2 \rangle B_{5/2}^2(x) \right. \right. \\ &\quad \left. \left. - \frac{8125}{2772} A_4^0 \langle r^4 \rangle B_{5/2}^4(x) \right] \right\}. \end{aligned} \quad (25)$$

At higher fields $m_{\perp} \equiv 1$.

Equations (21)–(25) in combination with empirical formulas for $M_{\text{Fe}}(T)$ and $K_{\text{Fe}}(T)$ (16) provide a direct analytical algorithm for computing $m_{\perp}(B)$, $B_a(T)$ and $B'_a(T) \equiv 2K_1/M_s$ proceeding from the CF parameters A_2^0 and A_4^0 . Although a nonzero A_4^3 is allowed by the symmetry, in the linear approximation it does not affect the anisotropy energy.⁹

Thus the dotted curves in Figs. 2 and 3 represent the $m_{\perp}(B)$, $B_a(T)$, and $B'_a(T)$ dependences calculated using the above algorithm with $A_2^0 = -333Ka_0^{-2}$ and $A_4^0 = 0.84Ka_0^{-4}$ (model 3). It is evident from Fig. 3 that in $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ J mixing is the main contributor to the breakdown of the linear theory, especially at high temperatures, where the gap between the dashed and the dotted curves of Fig. 3 practically disappears. Therefore, for those materials where J -mixing is inessential, one can expect a much better performance of the linear theory, par-

ticularly at high temperatures, which are important for applications.

C. Linear model with effective CF parameters

It has been demonstrated that J mixing plays an important role in governing the magnetic properties of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ at all temperatures; at low temperatures this is also true of the intramultiplet nonlinear effects. Therefore direct use of model 3 for practical purposes is out of the question. In this subsection we aim at demonstrating that the above analytical algorithm can indeed be utilized, however, if the CF parameters are suitably rescaled.

We chose $A_2^0 = -453Ka_0^{-2}$ and $A_4^0 = 128Ka_0^{-4}$ as effective CF parameters and used the same linear algorithm (21)–(25). We call this calculation procedure model 4. The results are presented by dash-dotted lines in Figs. 2 and 3. They agree with both model 1 and the experimental data better than either models 2 or 3. The agreement is good at all temperatures and magnetic fields save the region of low temperatures, where both B_a and B'_a are underestimated (Fig. 3).

Thus, for most applications model 4 appears to be nearly as accurate as model 1, but simpler and much less demanding for computing capacity. The price however is that the effective CF parameters cannot be expected to reproduce correctly the scheme of samarium energy levels which might be deduced independently from an absorption or inelastic-scattering experiment.

It also has to be noted that because $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ usually comes in form of powder samples with $0 < \delta < 0.8$, the models under review may need some generalization to allow for magnetic texture and nonuniform distribution of the interstitial nitrogen. For this purpose model 4 appears advantageous because it is fully analytical.

Finally, model 4 is advantageous also because it directly represents the free energy in the form of Eq. (20), the first two terms being the magnetocrystalline anisotropy energy [in a more general case there must be three terms, cf. (1)]. Such representation is convenient for many applications. However models 1 and 2 calculate the function $F(\theta)$ numerically; at low temperatures this function often has sharp cusps (see, e.g., Fig. 8 of Ref. 27) which means that $F(\theta)$ is irrepresentable as (1). In other words, at low temperatures the series

$$F = \sum_{n=1}^{\infty} K_n \sin^{2n}\theta \quad (26)$$

converges very slowly or even diverges. Strictly speaking, anisotropy constants for (1) cannot be calculated more accurately than in the linear approximation. Higher orders in perturbation theory lead to high-order terms in expansion (26), see Sec. II. Truncation of (26) after $n=3$ reduces the accuracy to that of the linear model and makes the rigorous calculation of $F(\theta)$ pointless. Thus for exchange-dominated systems the breakdown of the linear approximation means inapplicability of expression (1) for anisotropy energy. When this takes place, the full function $F(\theta)$ should generally be used, not its expansion up to $\sin^6\theta$. However, no such difficulty occurs when model 4 is used.

V. CONCLUSION

The linear theory of magnetocrystalline anisotropy in most $3d-4f$ intermetallics used for permanent magnets is a rather poor approximation. Higher-order terms and J mixing for the case of samarium should be taken into consideration. Consequences include the appearance of singularities in the free energy that cannot be represented by expression (1). However, the simple linear theory can be retained as a fair approximation if effective CF parameters are adopted. For $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ the CF parameters deduced from high-field magnetization data in the rigorous model are $A_2^0 = -333Ka_0^{-2}$, $A_4^0 = 0.84Ka_0^{-4}$ whereas corresponding effective CF parameters are $A_2^0 = -453Ka_0^{-2}$ and $A_4^0 = 128Ka_0^{-4}$. The theory with effective CF parameters has the virtue that the temperature dependence of the anisotropy constants and hence the magnetization curves can be represented in the form of analytical expressions involving generalized Brillouin functions. However, it does not reproduce the energy level scheme for the rare earth, which may be accessible to direct experimental measurements.

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*Present address: Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Zaragoza, Plaza San Francisco S/N, 50009 Zaragoza, Spain.

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