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Linear theory of magnetocrystalline anisotropy in $3d$-$4f$ intermetallics: A generalization to J-mixing compounds

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It is known that the magnetocrystalline anisotropy of a rare-earth–transition-metal intermetallic compound can be described by means of analytical expressions under the assumptions of the linear theory. These assumptions are that the spin-orbit interaction of the considered rare-earth ion is much stronger than the exchange interaction between the $3d$ and the $4f$ sublattices (so that mixing of states with different J is not allowed), and that the crystal-field potential can be treated as a small perturbation with regards to the mentioned exchange interaction. In this work, a generalization of the linear theory is proposed for compounds where the J mixing cannot be neglected (typically those based on light rare-earths such as Pr, Nd, and especially Sm). This is done by applying a suitable unitary transformation to the single-ion Hamiltonian describing the quantum state of the rare-earth ions, so that an effective description in terms of an isolated J multiplet can be retained, while at the same time the J-mixing effects are properly accounted for. Analytical expressions have therefore been obtained for the free energy of light-rare-earth-based magnetic materials and have been applied to interpret available experimental data on Sm_2Co_{17}.

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I. INTRODUCTION AND MOTIVATIONS

Intermetallic compounds based on transition metals (TM) and light rare earths (RE's), such as Sm_2Co_{17} and $Nd_2Fe_{14}B$, are the basic constituents of the best commercially available permanent magnets.[1] Although the interplay between the two sublattices (RE and TM) often gives rise to a complex and peculiar phenomenology for these alloys, the basic mechanisms which generate their properties are well understood: the $3d$ sublattice provides a high value of the saturation magnetization and a high Curie temperature, so that these materials can operate above room temperature (RT) without any significant loss of performance; conversely, the strong magnetocrystalline anisotropy is provided by the crystal field (CF) acting on the $4f$ electronic shell. Despite that, a complete analytical description of these systems is possible only in a few cases. The linear theory[2] allows one to find an explicit expression for the free energy due to the RE sublattice, and therefore to calculate analytically any physical quantity of interest, under two hypotheses: (1) the strength of the CF potential is small with respect to the $3d$-$4f$ exchange interaction and (2) the spin-orbit gap between the RE multiplets is large enough that the ground J multiplet is well isolated. While the first requirement is often satisfied by the RE-TM compounds of pratical interest, the relatively small spin-orbit interaction of light RE ions gives rise to non-negligible J-mixing effects. For example, it is known that the Sm^{3+} ion has a small gap (1435 K) between the ground and the first excited J multiplet. Due to this fact, the strong exchange field causes states belonging to different spin-orbit multiplets to mix heavily, and the contributions of excited J multiplets are no longer negligible. J mixing has attracted the interest of many authors because it can make it difficult to interpret the CF energy levels of this rare earth, thus affecting many physical properties of Sm-based compounds[3–5] (including the magnetocrystalline anisotropy of intermetallic alloys). Pr^{3+} and Nd^{3+} also present J-mixing effects, although they are not as crucial as in the case of Sm^{3+}. The strong J mixing makes it necessary to perform numerical calculations which, albeit accurate, do not allow a direct comparison of the results with the phenomenological models used by the experimentalists to analyze their data; moreover, the main convenience in using analytical expressions is that they allow a more detailed physical comprehension of the role of every single parameter in the model.[6]

In this paper, it will be shown that the linear theory can be modified in order to include J-mixing effects, thus allowing one to obtain analytical expressions which can be readily compared with available experimental data for exchange-dominated RE-TM systems. The described analytical model will be applied to study the temperature dependence of the magnetocrystalline anisotropy of Sm_2Co_{17} and compared with exact numerical results in order to test its reliability.

II. THE MODEL

The Hamiltonian[5] which describes the energy states of the RE ion in presence of spin-orbit interaction, RE-TM exchange interaction (treated in mean-field approximation), and CF potential is (symbols marked with a caret represent operators):

$$\hat{H}_{\mathrm{RE}}=\Lambda\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}+2\mu_B\mathbf{H}_{\mathrm{ex}}\cdot\hat{\mathbf{S}}+\hat{H}_{\mathrm{CF}}; \quad (1)$$

in this expression Λ is the spin-orbit coefficient, $\mathbf{H}_{\mathrm{ex}}$ is the exchange field, and $\hat{H}_{\mathrm{CF}}$ is the crystal-field Hamiltonian, which is expressed by means of tensor operators $\hat{C}_q^{(k)}$ as[7]

$$\hat{H}_{\mathrm{CF}}=\sum_{k,q} B_k^q\hat{C}_q^{(k)}, \quad (2)$$

where B_k^q are the CF parameters. The LS coupling used in Eq. (1) is justified by the fact that we will consider only the lowest multiplets of light RE ions such as Pr^{3+}, Nd^{3+}, and Sm^{3+}, for which this approximation is known to be valid.[8] The energy spectrum of the system is composed of multiplets separated by the isotropic spin-orbit coupling and split by the anisotropic interactions. If the interest is limited to properties involving only the ground manifold, the system can be described as a J multiplet and the Hamiltonian $\hat{H}_{\mathrm{RE}}$ can be replaced by an effective Hamiltonian

$$\hat{H}_{\mathrm{RE}}^{(J)}=2(g_J-1)\mu_B\mathbf{H}_{\mathrm{ex}}\cdot\hat{\mathbf{J}}+\hat{H}_{\mathrm{CF}}^{(J)} \tag{3}$$

written in terms of the total angular momentum operator $\hat{\mathbf{J}}$, provided the spin-orbit gap is large compared to the matrix elements of the other interactions. In this frame, $\hat{H}_{\mathrm{CF}}$ is replaced by

$$\hat{H}_{\mathrm{CF}}^{(J)}=\sum_{k,q} B_k^q\Theta_k\hat{C}_q^{(k)}(\hat{\mathbf{J}}), \tag{4}$$

where $\hat{C}_q^{(k)}(\hat{\mathbf{J}})$'s are written[2] in terms of $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$, and Θ_k are the Stevens' multiplicative factors[5] ($\Theta_2=\alpha_J$, $\Theta_4=\beta_J$, and $\Theta_6=\gamma_J$). Note that the Hamiltonians which can be used only in the restricted subspace consisting of the ground J multiplet have been labeled with the superscript (J).

The linear theory of the magnetocrystalline anisotropy[2] consists in calculating the first-order contribution to the free energy due to the RE ion. First, the RE Hamiltonian (3) is rewritten in a rotated reference frame in order to align the exchange field $\mathbf{H}_{\mathrm{ex}}$ with the z axis; then, the first-order contribution to the anisotropy energy are calculated by replacing the operators appearing in $\hat{H}_{\mathrm{CF}}^{(J)}$ with their thermal averages taken over the zeroth order eigenstates (those of the exchange-field Hamiltonian $|J,M\rangle$, with $E_M=2|g_J-1|\mu_B H_{\mathrm{ex}}M$). In order to represent these averages in a simple and compact form, generalized Brillouin functions $B_J^k(x)$ are defined so that

$$\begin{aligned}J^kB_J^k(x)&=\langle\hat{C}_0^{(k)}(\hat{\mathbf{J}})\rangle\\&=\frac{\sum_{M=-J}^{+J}\langle J,M|\hat{C}_0^{(k)}(\hat{\mathbf{J}})|J,M\rangle\exp(-E_M/k_BT)}{\sum_{M=-J}^{+J}\exp(-E_M/k_BT)},\end{aligned} \tag{5}$$

where $x=2J|g_J-1|\mu_BH_{\mathrm{ex}}/(k_BT)$ and k_B is the Boltzmann constant (notice that $\langle\hat{C}_q^{(k)}(\hat{\mathbf{J}})\rangle\equiv0$ when $q\neq0$). A survey on the most important properties of these functions is given in Ref. 2.

Unfortunately, in light RE ions the spin-orbit interaction is relatively weak and the above approximation is not adequate to describe many physical properties of these systems. We propose the use of a perturbative technique reported in Ref. 9, based on the effective Hamiltonian theory,[10,11] in order to include in $\hat{H}_{\mathrm{CF}}^{(J)}$ the so far neglected J-mixing effects. In a recent paper, this approach has been successfully used to study the magnetic anisotropy in single-molecule magnets.[12]

Using as basis vectors the eigenvectors of the spin-orbit operator $|\alpha JM\rangle$, the Hamiltonian matrix $\hat{H}_{\mathrm{RE}}$ can be rewritten as the sum of three terms:

$$\hat{H}_{\mathrm{RE}}=\Lambda\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}+\hat{H}_1+\hat{H}_2. \tag{6}$$

In the above equation $\hat{H}_1$ has nonzero matrix elements only inside the diagonal blocks and does not connect states with different α,J (i.e., different J multiplets), while $\hat{H}_2$ is different from zero only in the off-diagonal blocks and is the term responsible for J mixing. The technique described below takes advantage from an unitary transformation, which changes the original matrix $\hat{H}_{\mathrm{RE}}$ into a new one having very small matrix elements in the off-diagonal blocks. Diagonal elements are modified too, but the advantage of this approach is noteworthy: in the new basis, states belonging to different multiplets are almost uncoupled and the system can still be described as an effective J multiplet.

As it is formally shown in Ref. 9, it is possible to find an Hermitian operator Ω such that the matrix elements of $\hat{H}_{\mathrm{RE}}$ in the off-diagonal blocks calculated over the transformed set of vectors $e^{i\Omega}|\alpha JM\rangle$ are small enough to be neglected. This is equivalent to looking for a transformed Hamiltonian

$$\hat{H}'_{\mathrm{RE}}=e^{-i\Omega}\hat{H}_{\mathrm{RE}}e^{i\Omega}, \tag{7}$$

whose matrix elements between states with different α,J are much smaller than those of $\hat{H}_{\mathrm{RE}}$. Inside the J manifolds

$$\begin{aligned}&\langle\alpha JM|\hat{H}'_{\mathrm{RE}}|\alpha JM'\rangle\\&\quad=E_{0\alpha J}+\langle\alpha JM|\hat{H}_1|\alpha JM'\rangle\\&\qquad-\sum_{\alpha''J''M''}\frac{\langle\alpha JM|\hat{H}_2|\alpha''J''M''\rangle\langle\alpha''J''M''|\hat{H}_2|\alpha JM'\rangle}{E_{0\alpha''}J''-E_{0\alpha J}}\end{aligned} \tag{8}$$

where $E_{0\alpha J}$ are the eigenvalues of the spin-orbit operator.

In order to illustrate our approach, we first consider the simple case of a system characterized by an uniaxial crystal field parallel to the exchange field $\mathbf{H}_{\mathrm{ex}}$. Choosing the z axis parallel to the molecular field and limiting to the second order for $\hat{H}_{\mathrm{CF}}$, it is

$$\hat{H}_{\mathrm{RE}}=\Lambda\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}+2\mu_BH_{\mathrm{ex}}\hat{S}_z+B_2^0\hat{C}_0^{(2)}, \tag{9}$$

where the spin operator $\hat{S}_z$ is the zeroth component of the rank one irreducible tensor operator $S^{(1)}$.[13] Furthermore, the ground J multiplet is assumed to be followed by a first excited manifold of total angular momentum $J+1$, as in the case of Pr^{3+}, Nd^{3+}, and Sm^{3+}. In fact, by numerical diagonalization we found that the average contribution of other excited multiplets in the calculation of the ground state energy levels is negligible for our purposes (below 2% for Sm^{3+}, and less than 1% for other rare earths). Although in principle it is possible to include the effects of these manifolds in our model, this would lead to complications in the formalism which are not needed in this case. Employing Eq. (8) and applying the Wigner-Eckart theorem, we can evaluate the matrix elements of $\hat{H}'_{\mathrm{RE}}$ in the J multiplet:

$$\begin{aligned}\langle JM|\hat{H}'_{\mathrm{RE}}|JM'\rangle ={}& E_{0J}+\langle JM|\hat{H}_1|JM'\rangle+\frac{(2\mu_B H_{\mathrm{ex}})^2}{\Delta_{\mathrm{SO}}}\sum_{M''}(-1)^{2J-M-M''}\langle J\|S^{(1)}\|J+1\rangle^2\begin{pmatrix} J & 1 & J+1\\ -M & 0 & M''\end{pmatrix}\begin{pmatrix} J+1 & 1 & J\\ -M'' & 0 & M'\end{pmatrix}\\ &+\frac{2\mu_B H_{\mathrm{ex}}B_2^0}{\Delta_{\mathrm{SO}}}\sum_{M''}(-1)^{2J-M-M''}\langle J\|S^{(1)}\|J+1\rangle\langle J\|C^{(2)}\|J+1\rangle\left[\begin{pmatrix} J & 1 & J+1\\ -M & 0 & M''\end{pmatrix}\begin{pmatrix} J+1 & 2 & J\\ -M'' & 0 & M'\end{pmatrix}\right.\\ &\left.+\begin{pmatrix} J & 2 & J+1\\ -M & 0 & M''\end{pmatrix}\begin{pmatrix} J+1 & 1 & J\\ -M'' & 0 & M'\end{pmatrix}\right]\end{aligned}\tag{10}$$

where $\Delta_{\mathrm{SO}}=E_{0J+1}-E_{0J}$ is the spin-orbit gap between the ground manifold and the first excited manifold, ( ) are $3j$ symbols[14] and $\langle\|\ \|\rangle$ are reduced matrix elements. In Eq. (10) a term quadratic in $\hat{H}_{\mathrm{CF}}$ has been neglected because in these intermetallic compounds the strenght of CF potential is generally small with respect to the exchange interaction. Since the two last terms in the preceding equation are divided by Δ_{SO}, the effects of J mixing can be neglected if the two considered multiplets are well separated in energy.

Exploiting the angular momentum properties, it is possible to express the linear combination of products of $3j$ symbols appearing in Eq. (10) as matrix elements of $\hat{C}_q^{(k)}(\hat{\mathbf{J}})$ operators; in the present case, apart from constant additive terms which only represent a uniform energy shift, it is

$$\begin{aligned}&\sum_{M''}(-1)^{2J-M-M''}\begin{pmatrix} J & 1 & J+1\\ -M & 0 & M''\end{pmatrix}\begin{pmatrix} J+1 & 1 & J\\ -M'' & 0 & M'\end{pmatrix}\\ &\quad=\frac{2}{3(1+2J)(1+J)(3+2J)}\langle JM|\hat{C}_0^{(2)}(\hat{\mathbf{J}})|JM'\rangle\end{aligned}\tag{11}$$

and

$$\begin{aligned}&\sum_{M''}(-1)^{2J-M-M''}\left[\begin{pmatrix} J & 1 & J+1\\ -M & 0 & M''\end{pmatrix}\begin{pmatrix} J+1 & 2 & J\\ -M'' & 0 & M'\end{pmatrix}\right.\\ &\qquad\left.+\begin{pmatrix} J & 2 & J+1\\ -M & 0 & M''\end{pmatrix}\begin{pmatrix} J+1 & 1 & J\\ -M'' & 0 & M'\end{pmatrix}\right]\\ &\quad=\frac{-4\sqrt{3}}{5\sqrt{J}\sqrt{2+J}(3+11J+12J^2+4J^3)}\langle JM|\hat{C}_0^{(3)}(\hat{\mathbf{J}})|JM'\rangle\\ &\qquad-\frac{2J^2+7J+6}{2}\langle JM|\hat{C}_0^{(1)}(\hat{\mathbf{J}})|JM'\rangle.\end{aligned}\tag{12}$$

The effective Hamiltonian then becomes

$$\hat{H}^{(J)}=2(g_J-1)\mu_B\mathbf{H}_{\mathrm{ex}}\cdot\hat{\mathbf{J}}+\hat{H}_{\mathrm{CF}}^{(J)}+\hat{H}_{\mathrm{mixing}},\tag{13}$$

where

$$\begin{aligned}\hat{H}_{\mathrm{mixing}}={}&\frac{(2\mu_B H_{\mathrm{ex}})^2}{\Delta_{\mathrm{SO}}}\frac{2}{3(1+2J)(1+J)(3+2J)}\hat{C}_0^{(2)}(\hat{\mathbf{J}})\\ &+\frac{2\mu_B H_{\mathrm{ex}}B_2^0}{\Delta_{\mathrm{SO}}}\frac{-4\sqrt{3}}{5\sqrt{J}\sqrt{2+J}(3+11J+12J^2+4J^3)}\\ &\times\left[\hat{C}_0^{(3)}(\hat{\mathbf{J}})-\frac{2J^2+7J+6}{2}\hat{C}_0^{(1)}(\hat{\mathbf{J}})\right].\end{aligned}\tag{14}$$

The fact that operators of odd order (which are not usually present) appear in the effective Hamiltonian is not surprising; in fact, as their coefficients are linear in the exchange field H_{ex}, the corresponding spherical operators must be odd as well, so that the necessary invariance under time-reversal is guaranteed.[10] If the Hamiltonian $\hat{H}_{\mathrm{RE}}$ contains more terms or if there are several multiplets whose mixing with the ground manifold cannot be neglected, the procedure is the same developed above, but more terms have to be added to $\hat{H}_{\mathrm{mixing}}$.

III. EXPLICIT EXPRESSIONS FOR ANISOTROPY CONSTANTS: THE EFFECTS OF *J* MIXING

As stated above, one of the main advantages of the linear theory with respect to numerical calculations is the possibility to obtain analytical expressions for the physical quantities of interest, which can be readily used to analyze experimental data. For example, the usual phenomenological expression for the magnetic anisotropy free energy of RE-TM compounds with 2:17 stoichiometry is

$$F=K_1\sin^2\theta+K_2\sin^4\theta+K_3\sin^6\theta+K'_3\sin^6\theta\cos 6\phi.\tag{15}$$

In principle, this expression should be written as the sum of infinite terms in $\sin^{2n}\theta$ (Ref. 15); however, the series is often truncated up to the sixth order, neglecting anisotropy constants K_n with $n>3$. Kuz'min[2] has shown that, in absence of J mixing and within the framework of the linear theory, Eq. (15) is the exact expression for the free energy, and has given analytical expressions for the temperature dependence of the four anisotropy constants. This can be generalized to the case where J mixing is not negligible, by analyzing the angular dependence of the free energy calculated in Sec. II; it is found that the higher-order corrections to Eq. (15) are proportional to $B_J^7(x)$ with a small numerical coefficient if the main hypothesis of the linear theory (i.e., the CF potential can be regarded as a perturbation with respect to the exchange interaction) is applicable. This means that eight-order anisotropy constants due to J-mixing effects are always negligible for all rare earths, and equal to zero in the particular case of samarium. Equation (15) can then be safely used to interpret the experimental data for any exchange-dominated intermetallic compound.

Within the framework of the linear theory, the analytical expressions for the anisotropy constants appearing in Eq. (15) are

$$\begin{aligned}K_1=&\Big\{-\frac{3}{2}\Theta_2J^2B_J^2(x)-3\sqrt{3}\delta_2\frac{2\mu_BH_{\rm ex}}{\Delta_{\rm SO}}[-2J^3B_J^3(x)\\&+(2J^2+7J+6)JB_J^1(x)]\Big\}B_2^0\\&+\Big\{-5\Theta_4J^4B_J^4(x)-20\sqrt{10}\delta_4\frac{2\mu_BH_{\rm ex}}{\Delta_{\rm SO}}[-2J^5B_J^5(x)\\&+(2J^2+11J+15)J^3B_J^3(x)]\Big\}B_4^0\\&+\Big\{-\frac{21}{2}\Theta_6J^6B_J^6(x)-4\sqrt{21}\delta_6\frac{2\mu_BH_{\rm ex}}{\Delta_{\rm SO}}[-74J^7B_J^7(x)\\&+21(2J^2+15J+28)J^5B_J^5(x)]\Big\}B_6^0,\end{aligned}\tag{16}$$

$$\begin{aligned}K_2=&\Big\{\frac{35}{8}\Theta_4J^4B_J^4(x)+35\delta_4\sqrt{\frac{5}{2}}\frac{2\mu_BH_{\rm ex}}{\Delta_{\rm SO}}[-2J^5B_J^5(x)\\&+(2J^2+11J+15)J^3B_J^3(x)]\Big\}B_4^0\\&+\Big\{\frac{189}{8}\Theta_6J^6B_J^6(x)+27\delta_6\sqrt{21}\frac{2\mu_BH_{\rm ex}}{\Delta_{\rm SO}}[-46J^7B_J^7(x)\\&+7(2J^2+15J+28)J^5B_J^5(x)]\Big\}B_6^0,\end{aligned}\tag{17}$$

$$\begin{aligned}K_3=&\Big\{-\frac{231}{16}\Theta_6J^6B_J^6(x)-\frac{33}{2}\delta_6\sqrt{21}\frac{2\mu_BH_{\rm ex}}{\Delta_{\rm SO}}\\&\times[-110J^7B_J^7(x)+7(2J^2+15J+28)J^5B_J^5(x)]\Big\}B_6^0,\end{aligned}\tag{18}$$

$$\begin{aligned}K_3'=&\Big\{\frac{\sqrt{231}}{16}\Theta_6J^6B_J^6(x)+\frac{3}{2}\delta_6\sqrt{11}\frac{2\mu_BH_{\rm ex}}{\Delta_{\rm SO}}[38J^7B_J^7(x)\\&+7(2J^2+15J+28)J^5B_J^5(x)]\Big\}B_6^6;\end{aligned}\tag{19}$$

where

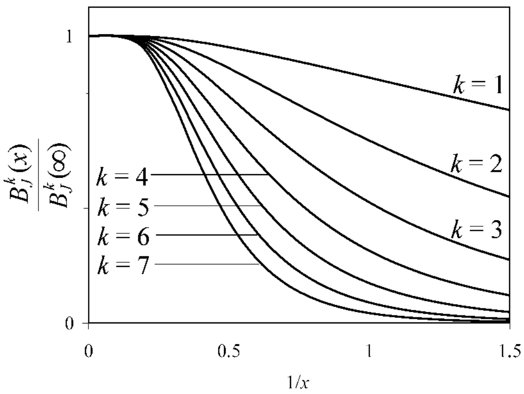

FIG. 1. Thermal averages of generalized Brillouin functions $B_J^k(x)$, calculated within the linear theory ($J=4$).

$$\delta_k=-\frac{\langle J\|S^{(1)}\|J+1\rangle\langle J\|C^{(k)}\|J+1\rangle\sqrt{2^{k+1}}}{(2k+1)\sqrt{(J+1)(2J+1)(2J+3)}\prod_{l=2-k}^{2+k}\sqrt{2J+l}}.\tag{20}$$

If the Stevens factor Θ_k does not vanish within the ground state, it is possible to obtain a simpler expression for the δ_k coefficients, which in the case of light rare earths ($J=L-S$) is

$$\delta_k=\frac{\Theta_kS\sqrt{2^{1-k}k(k+1)}}{(2k+1)(2J+k+2)(J+1)}.\tag{21}$$

It is straightforward to show that Eqs. (16)–(19) are reduced to the corresponding expressions calculated in absence of J-mixing effects[2] by taking the limit for $\Delta_{\rm SO}\to\infty$; in fact, it can be noticed that the terms containing even-order generalized Brillouin functions are the same as in Ref. 2, while J mixing adds the odd-order terms which are all multiplied by a factor $\mu_BH_{\rm ex}/\Delta_{\rm SO}$. Figure 1 shows the temperature dependence of the generalized Brillouin functions for $J=4$; explicit expressions of $B_J^n(x)$ for $1\leqslant n\leqslant 7$, in terms of elementary functions, are given in the Appendix. The behavior at high temperatures can be studied by neglecting all the generalized Brillouin functions of order higher than the second;[16] in this case, $K_2=K_3=K_3'=0$, and K_1 only depends on the CF parameter B_2^0:

$$K_1=-\frac{3}{2}\Theta_2B_2^0\left[J^2B_J^2(x)+\frac{3}{5}\frac{2\mu_BH_{\rm ex}S}{\Delta_{\rm SO}}\frac{J(2J+3)}{J+1}B_J^1(x)\right].\tag{22}$$

Expanding Eq. (22) in power series and keeping the leading terms results in

$$\begin{aligned}K_1=&\frac{3(2J+3)J}{2(J+1)}S^2\Theta_2B_2^0(2\mu_BH_{\rm ex})^2\left[\frac{1}{5\Delta_{\rm SO}}(k_BT)^{-1}\right.\\&\left.+\frac{(2J-1)}{60}(k_BT)^{-2}\right],\end{aligned}\tag{23}$$

which turns out to be a simple and compact expression for the anisotropy constant K_1 in the high-temperature limit.

IV. THE MAGNETOCRYSTALLINE ANISOTROPY OF Sm_2Co_{17}

In order to show how the free-energy expression derived in the previous section can be directly compared with experimental data, the case of Sm_2Co_{17} will be considered. The crucial role of *J*-mixing effects for this compound has already been studied with numerical calculations during the last years;[17] in particular, the sixth-order contributions to the anisotropy within the ground ($J=5/2$) multiplet are zero, thus the measured basal-plane anisotropy is entirely due to *J*-mixing effects.[17] It will be shown that the model presented in this paper allows a straightforward determination of the CF parameters for Sm^{3+} in this compound, and a better comprehension of their physical role.

Sm_2Co_{17} presents an axial arrangement of the easy magnetization direction (EMD) in the whole temperature range from liquid helium to the Curie temperature ($T_C \simeq 1200$ K). Its anisotropy field (defined as the minimum value of the applied magnetic field needed to saturate the sample magnetization) was experimentally measured at different temperatures[17] by magnetizing the sample towards both the "hard" directions in the basal plane. No magnetic field-induced transitions were detected. It is possible to show that, in absence of first-order magnetization processes (FOMP's),[18] the anisotropy field H_A for the two directions *x*, *y* parallel to the EMD (thereby defined as the *z* axis) is

$$H_A^{(x,y)} = \frac{2K_1 + 4K_2 + 6K_3 \pm 6K_3'}{M_S}, \tag{24}$$

where M_S is the magnetization value at the saturation. From the measured anisotropy field, it is then possible to derive

$$2K_1 + 4K_2 + 6K_3 = \frac{H_A^{(x)} + H_A^{(y)}}{2} M_S \tag{25}$$

and

$$K_3' = \frac{H_A^{(x)} - H_A^{(y)}}{12} M_S . \tag{26}$$

The experimental values of these quantities at different temperatures were then fitted to their analytical expressions, calculated by means of Eqs. (16)–(19); it must be noted that $\Theta_6 = 0$ for the ground multiplet of Sm^{3+}, therefore the value $\delta_6 = -5 \times 17/(3^4 \times 7 \times 11^2 \times 13^2 \times 21)^{1/2}$ had to be calculated directly using Eq. (20). The contribution of the cobalt sublattice to the free energy was estimated from the anisotropy field measurement of Y_2Co_{17} (Ref. 19) and subtracted from Eq. (25). The spin-orbit gap Δ_{SO} was fixed at 1435 K (Ref. 20). The exchange interaction parameter $2\mu_B H_{ex}$ was fixed at 360 K (at $T=0$ K), following the results of inelastic neutron scattering experiments;[21] the temperature dependence of the exchange field was supposed to be the same as the bulk magnetization of the material. This is a common procedure, whose applicability was accurately checked by means of inelastic neutron scattering in the case of Sm_2Fe_{17} (Ref. 25); however, in the temperature range which we are interested in (78–300 K), the variation of the bulk magnetization is less than 4%, so that the decrease of the exchange field value is not very significant. Once H_{ex} is known, the value of $2K_1 + 4K_2 + 6K_3$ calculated within the linear theory does not depend on the CF parameter B_6^6, while the basal-plane anisotropy constant K_3' depends only on B_6^6. This is a direct, analytical confirmation of a behavior which was inferred with numerical calculations: namely, the value of K_3' calculated by diagonalization of the entire matrix corresponding to the *J*-mixing Hamiltonian (1) is almost independent of the axial CF parameters B_K^0 (Ref. 17).

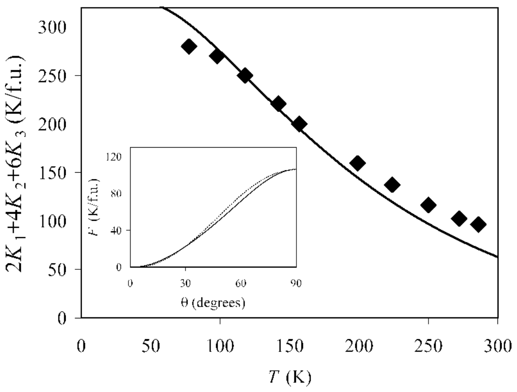

FIG. 2. Comparison between the experimental (diamonds) and calculated (line) values of $2K_1 + 4K_2 + 6K_3$ for Sm_2Co_{17}. Inset: comparison between the θ dependence of the anisotropy free energy calculated by our analytical approach (continuous line) and by numerical diagonalization of Eq. (1) (dotted line) at $T=78$ K.

The experimental data were fitted to their corresponding expressions [Eqs. (25) and (26)] by freely varying the four CF parameters. Good results are obtained (Figs. 2 and 3) with $B_2^0 = -290 \pm 30$ K, $B_4^0 = -200 \pm 70$ K, $B_6^0 = -400 \pm 100$ K, and $B_6^6 = \pm(800 \pm 100)$ K (this procedure leaves the sign of B_6^6 undetermined). These parameters allow one to interpret the reported magnetic data, and are consistent with those deduced by the analysis of the observed neutron transitions.[21] By examining the FOMP diagrams in Ref. 18, it is found that the values of the anisotropy constants calculated with these parameters are such that no field-induced

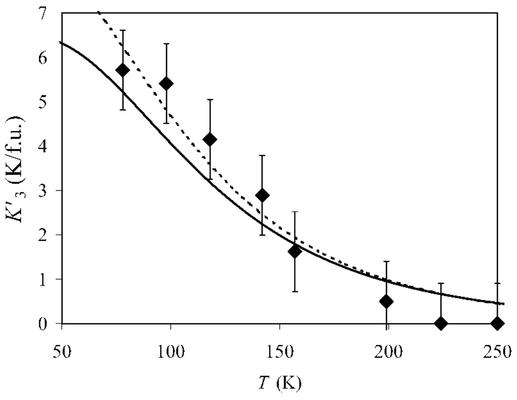

FIG. 3. Temperature dependence of the basal-plane anisotropy constant K_3'. Diamonds: experimental values. Continuous line: analytical calculations (see text). Dotted line: numerical calculations (after Ref. 17).

TABLE I. Comparison between the lowest energy levels (expressed in K) of Sm_2Co_{17} calculated with three different approaches: (a) no J mixing, (b) analytical model (this work), (c) exact numerical results. The last column shows the composition of the J-mixing eigenstates calculated with model (c).

model (a)	model (b)	model (c)	eigenstate
0	0	0	$0.982\|5/2,-5/2\rangle+0.190\|7/2,-5/2\rangle$
343	295	295	$-0.967\|5/2,-3/2\rangle-0.256\|7/2,-3/2\rangle$
618	578	568	$0.964\|5/2,-1/2\rangle+0.266\|7/2,-1/2\rangle$
875	804	782	$-0.948\|5/2,1/2\rangle-0.317\|7/2,1/2\rangle$
1115	1107	1055	$0.949\|5/2,3/2\rangle+0.317\|7/2,3/2\rangle$
1285	1304	1287	$-0.967\|5/2,5/2\rangle-0.254\|7/2,5/2\rangle$

transitions are predicted. This is a crucial requirement, since in presence of a FOMP Eq. (24) might not be the correct expression for the saturating magnetic field. Similar values of $H_{\rm ex}$ and B_2^0, resulting from fitting single-crystal magnetization curves, were also reported.[22] It must be noted that the obtained values of the CF parameters are strongly sensitive to a variation of the exchange field, as is expected in this class of ferromagnetic compounds for which the exchange interaction is much larger than the CF potential.

We will now test the applicability of the presented perturbative approach in the calculation of the energy spectra. Table I shows a comparison between the six lowest energy levels evaluated with the above parameters[23] (without any external applied field, so that the exchange field is parallel to the easy axis z) in three different ways: (a) by analytical determination[24] of the eigenvalues of Eq. (4) within the ground multiplet (not including J-mixing effects), (b) by analytical determination[24] of the eigenvalues of effective Hamiltonian $\hat{H}^{(J)}$ [Eq. (13)], (c) by numerical diagonalization of Eq. (1) within the ${}^6H_{5/2}+{}^6H_{7/2}$ manifolds (exact results). It can be noticed that, while neglecting J mixing leads to an average deviation of about 10% from the exact numerical values, the analytical approach described in Sec. II accounts for these effects with a residual discrepancy of about 2%. This offers a simple way to analyze the results of spectroscopic experiments, such as inelastic neutron scattering, along with other magnetic measurements. The only case where our analytical model does not improve the result of model (a) is that of the highest energy level [the fact that models (a) and (c) give almost the same results is coincidential]. The reason for that lies in the use of second order perturbation theory in Eq. (8): supposing that the exchange interaction is dominant with respect to the crystal field, the leading J-mixing term (quadratic in the exchange field) modifies the energy level scheme in such a way that the splitting between the lowest and the highest energy level cannot be corrected. However, this does not affect the calculation of physical quantities, since the above level is very high in energy (in our case, $>4RT$). The considerable effort of adding more high-order terms in Eq. (8) would give rise to very cumbersome equations, without improving our results; nevertheless, it may be worth for the analysis of spectroscopic transitions involving the highest energy level.

To ensure that the linear approximation is applicable, the axial part of the free energy $K_1\sin^2\theta+K_2\sin^4\theta+K_3\sin^6\theta$ (Fig. 2, inset) and the basal-plane anisotropy constant K_3' (Fig. 3) were compared with their values as calculated by numerical diagonalization of Eq. (1). The results are quite satisfactory: the free energy is reproduced with an average deviation smaller than 2%. The quantity $2K_1+4K_2+6K_3$ was also calculated by a numerical approach involving diagonalization of the 14×14 matrix representing $\hat{H}_{\rm RE}$ within the ${}^6H_{5/2}+{}^6H_{7/2}$ subspace, and fitted to the experimental data using the linear theory results as a starting point for the CF parameters. These calculations resulted in $B_2^0=-220\pm50$ K, $B_4^0=-150\pm100$ K, and $B_6^0=-400\pm100$ K; this result confirms the applicability of the linear theory for this compound.

A comparison of the parameters obtained in the present work with those previously reported in the literature is also possible. Ref. 26 reports a simplified analysis of magnetic data for Sm_2Co_{17}, obtaining $2\mu_BH_{\rm ex}=442$ K and $B_2^0=-208$ K; however, the value of B_2^0 is not very precise, due to the fact that the fourth- and sixth-order CF parameters are neglected and J-mixing effects are not considered. We performed a J-mixing linear theory analysis of our anisotropy data with the constraint $B_4^0=B_6^0=0$; however, we found that it is impossible to fit the low temperature part of the curve. In Ref. 21, the value $B_2^0=-280\pm160$ K, based on inelastic neutron scattering measurements, is given for Sm_2Co_{17}; this is in agreement with our results. The obtained B_6^6 parameter is about twice the numerically estimated value of -410 K (Ref. 17); however, this is mostly due to the fact that Ref. 17 uses a higher value for the exchange field $(2\mu_BH_{\rm ex}=442\text{ K})$. Using this parameter, the linear theory gives $|B_6^6|=550\pm100$ K; this is in line with the value reported in Ref. 17, which is affected by an error bar of the same magnitude. Therefore, the linear theory is proved to be a good approximation in this case. Moreover, the set of parameters we obtained for Sm^{3+} in this compound is in line with those derived by fitting the magnetization curves of R_2Co_{17}, with $R=$ Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er.[22] This fact supports the validity of our results. A comparison of the CF parameters in the above compounds with those of other isostructural intermetallic alloys is not straightforward, since significant variations are induced by changing the TM atoms, which cannot be accounted for in a simple way. For example, the leading crystal-field parameters B_2^0 shows a significant decrease in its absolute value when Mn or Fe atoms substitute Co in the TM sublattice of Sm_2Co_{17}, even changing its sign from negative to positive when the Fe composition reaches about 60%.[26] Also the crystal-field parameters reported[27] for Pr_2Zn_{17} (the Sm compound has not been studied), resulting from inelastic neutron scattering experiments, show a positive sign for this parameter. Recently, the effect of the TM sublattice on the crystal-field potential in some 1:12 compounds has been investigated by means of density functional calculations.[28]

V. CONCLUSIONS

A generalization of the linear theory for the magnetic anisotropy of exchange-dominated systems, which takes account of possible J-mixing effects, has been proposed. A unitary transformation was applied to the single-ion RE Hamiltonian, which was then rewritten on a reduced basis; in this framework, it is possible to take J-mixing effects into account while working on an effective, isolated manifold; the CF Hamiltonian includes additional operators, some of which are of odd order (and are not usually present). Some useful considerations can be made.

(1) The authors of Ref. 6 propose that the linear model in $Sm_2Fe_{17}N_3$ might take J-mixing effects into account by choosing rescaled effective values for the CF parameters appearing in the ground-state Hamiltonian $\hat{H}_{\mathrm{CF}}^{(J)}$. The model presented in Sec. II shows that this approach is not formally correct, since it does not take into account the contributions of the odd-rank terms generated by J mixing. These contributions have a peculiar temperature behavior which cannot be reproduced by varying the coefficients of even-rank operators, which are the only components of $\hat{H}_{\mathrm{CF}}^{(J)}$. Moreover, due to the fact that $\Theta_6=0$ for Sm^{3+}, rescaling the CF parameters B_2^0 and B_4^0 cannot generate sixth-order anisotropy contributions, which can be crucial for compounds such as Sm_2Co_{17} (for example, the basal-plane anisotropy constant K_3' would be zero at all temperatures). Lastly, diagonalization of $\hat{H}_{\mathrm{CF}}^{(J)}+\hat{H}_{\mathrm{mixing}}$ with the right values of the parameters should reproduce satisfactorily the energy-level scheme involved in the calculation of the anisotropy constants, while the approach described in Ref. 6 cannot do so in case of strong J mixing.

(2) The linear model allows to use the phenomenological free energy expression (15), neglecting terms of order higher then the sixth. Outside the boundaries of the linear theory, generation of significant highest-order anisotropy constant is possible,[6] but only if the CF potential cannot be regarded as a perturbation with respect to the exchange interaction; in this paper it has been shown that the J mixing cannot generate, by itself, appreciable terms of order higher than the sixth, and that Eq. (15) remains correct.

(3) Numerical calculations[17] allowed to infer that the presence of J-mixing results in a smoothing of the temperature dependence of $K_3'(T)$, which remains non-negligible at higher temperatures. An analytical explanation of this fact can now be given; while in absence of J-mixing effects the only contribution to K_3' is proportional to $B_J^6(x)$, for Sm^{3+} this constant has the same temperature dependence of $B_J^5(x)$. Since the generalized Brillouin functions satisfy the inequality

$$\frac{B_J^n(x)}{B_J^n(\infty)}>\frac{B_J^m(x)}{B_J^m(\infty)} \tag{27}$$

if $n<m$ (see Fig. 1), the observed behavior can be accounted for; not only the absolute magnitude, but also the temperature dependence of the anisotropy constants is strongly affected by J mixing.

APPENDIX: ANALYTICAL EXPRESSIONS OF THE GENERALIZED BRILLOUIN FUNCTIONS

The generalized Brillouin functions can be written in a simple analytical form, with the definition

$$B_J^n=A_n(\xi,\eta)+B_n(\xi,\eta)\coth\left(\frac{2J+1}{2J}x\right),$$

where $\xi=(1/2J)\coth(x/2J)$, $\eta=1/2J$, and $A_n(\xi,\eta)$ and $B_n(\xi,\eta)$ are the polynomial expressions given in the following:

$$A_1(\xi,\eta)=\xi,$$

$$B_1(\xi,\eta)=-(1+\eta),$$

$$A_2(\xi,\eta)=1+2\eta+3\xi^2,$$

$$B_2(\xi,\eta)=-3(1+\eta)\xi,$$

$$A_3(\xi,\eta)=3\xi[2-(-4+\eta)\eta+5\xi^2],$$

$$B_3(\xi,\eta)=(1+\eta)[-1+\eta(-2+3\eta)-15\xi^2],$$

$$\begin{aligned}A_4(\xi,\eta)={}&[1-4\eta(-1+\eta+4\eta^2)\\&+45\xi^2-45(-2+\eta)\eta\xi^2+105\xi^4],\end{aligned}$$

$$B_4(\xi,\eta)=5(1+\eta)\xi[-2+\eta(-4+9\eta)-21\xi^2],$$

$$\begin{aligned}A_5(\xi,\eta)={}&15\xi(1+\eta\{4+\eta[-7+\eta(-22+3\eta)]\}\\&+28\xi^2-14\eta(-4+3\eta)\xi^2+63\xi^4)\end{aligned}$$

$$\begin{aligned}B_5(\xi,\eta)={}&-(1+\eta)(1+\eta\{4+\eta[-14+9\eta(-4+5\eta)]\}\\&+105\xi^2-210\eta(-1+3\eta)\xi^2+945\xi^4),\end{aligned}$$

$$\begin{aligned}A_6(\xi,\eta)={}&[1+2\eta[3+2\eta(1+6\eta)(-5+16\eta^2)]\\&+105(2+\eta\{8+\eta[-20+\eta(-56+15\eta)]\})\\&\times\xi^2-4725[-1+2(-1+\eta)\eta]\xi^4+10395\xi^6],\end{aligned}$$

$$\begin{aligned}B_6(\xi,\eta)={}&-21(1+\eta)\xi(1+\eta\{4+\eta[-19+\eta(-46\\&+75\eta)]\}+60\xi^2-30\eta(-4+15\eta)\xi^2+495\xi^4),\end{aligned}$$

$$\begin{aligned}A_7(\xi,\eta)={}&7\xi\{4-\eta[-24+\eta(110+\eta\{600+\eta[-556+9\eta\\&(-264+25\eta)]\})]+225(2+\eta\{8+\eta[-26+\eta\\&(-68+27\eta)]\})\xi^2-4455[-2+\eta(-4+5\eta)]\xi^4\\&+19305\xi^6\},\end{aligned}$$

$$\begin{aligned}B_7(\xi,\eta)={}&(1+\eta)\{-1+\eta[-6+\eta(41+\eta\\&\times\{204+\eta[-463+225\eta(-6+7\eta)]\})]\\&-378\xi^2-189\eta\{8+\eta[-48+\eta(-112\\&+225\eta)]\}\xi^2+17325[-1+\eta(-2+9\eta)]\\&\times\xi^4-135135\xi^6\}.\end{aligned}$$

[1] For a review on this class of compounds, see for example K.H.J. Buschow, Rep. Prog. Phys. **54**, 1123 (1991), and references therein.

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[23] In order to test the reliability of our model, the similarity between the exact and the approximate energy levels was tested with different sets of parameters, always with positive results.

[24] In the simple case where all B_k^q with $q \neq 0$ are zero and the exchange is parallel to the z axis, the 6×6 matrix describing the ground state of Sm^{3+} is diagonal on the $|J,M\rangle$ basis, both with and without adding $\hat{H}_{\mathrm{mixing}}$.

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