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Basal-plane anisotropy for Sm_2Co_{17}: The crucial role of J mixing

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The sixth-order basal-plane anisotropy constant K_3' was deduced at different temperatures for Sm_2Co_{17}. The values were derived from measurements of the anisotropy field H_A performed along the two hard directions corresponding to the crystallographic a and b axes. In the frame of a single-ion model with exchange and crystal field, K_3' is proportional to the sixth-order crystal-field term. However, the sixth-order term is zero for the Sm^{3+} ion within the ground state multiplet. The experimental data were then compared with a curve $K_3'(T)$ calculated considering the three lowest-lying J multiplets. Using perturbation theory it was shown that K_3' is directly proportional to the sixth-order crystal-field parameter B_{66} even in the case of strong J mixing due to the exchange field. The best fit of the experimental data was obtained by means of a set of parameters which are consistent with those given in the literature, and in particular an accurate determination of B_{66} was possible. The results of the theoretical calculation were also compared with anisotropy field measurements on the isostructural compound Er_2Co_{17}, for which the J mixing is not expected to be significant.

I. INTRODUCTION

Rare-earth–transition-metal (RE-TM) intermetallic compounds with TM = Co, Fe are an important class of materials because of their outstanding magnetic properties. In particular they show a strong magnetocrystalline anisotropy (MCA) which is mainly produced by RE ions as a consequence of the crystal field (CF) acting on the $4f$ electrons. In addition the TM sublattice, which is responsible for the large magnetic moment and high Curie temperatures characteristic of RE-TM compounds,[1,2] also supplies a relevant contribution to the anisotropy, which is dominant at high temperatures. Of special interest has been the 2:17 family of compounds and particularly the easy-axis Sm_2Co_{17}, which is the basic constituent of one of the most complex and powerful permanent magnets.[3] Given the interest in applications, the rhomboedral ($R\overline{3}m$) Sm_2Co_{17} compound has been extensively studied during the last decades. However, also due to the lack of single-crystal samples, some questions are still open: for example the accurate determination of high-order anisotropy terms[4] and a quantitative evaluation of the J-mixing effects for Sm^{3+} $4f$ multiplets. In fact it is known that Sm^{3+} ion has a small gap (about 1400 K) between the $^6H_{5/2}$ (fundamental) and the $^6H_{7/2}$ (first excited) multiplets. For this reason, Sm compounds may show particular properties due to the mixing of states belonging to different J manifolds.[2,5] After the first successful attempts to treat the MCA of RCo_5 and R_2Co_{17} compounds in the frame of a single-ion model with exchange and crystal field,[6] J-mixing calculations performed on $SmCo_5$ showed a fair agreement with experiments.[7,8] The single-ion nature of the MCA in these compounds was confirmed and the existence of sixth-order anisotropy of the samarium ions sublattice, which cannot be accounted for considering only the ground multiplet,[7,9] was suggested. However, the available experimental data were not accurate enough to confirm this hypothesis. An attempt was made to treat the basal-plane anisotropy of the Sm sublattice in $(Sm_xY_{1-x})_2Co_{17}$ in the frame of a two-multiplet system,[10] but no quantitative agreement with the experimental data was found. Later on, a study of the magnetic properties of $R_2Fe_{14}B$ (R = Sm, Nd, Pr) has revealed that sixth-order CF terms and excited J multiplets contributions are indispensable to explain some anomalous properties of the anisotropy in these compounds.[11]

In the present work the basal-plane anisotropy of Sm_2Co_{17} was measured and the sixth-order anisotropy constant K_3' (which is only due to the RE sublattice) was deduced. It was then shown that the results of a theoretical calculation based on the single-ion model are quantitatively consistent with the experimental data if J-mixing effects on the Sm^{3+} lowest electronic levels are considered. In this frame the value of the sixth-order crystal field parameter B_{66}, which was shown to be proportional to K_3', was derived. The results of the theoretical calculation were also compared with anisotropy field measurements on the isostructural compound Er_2Co_{17}, for which the J mixing is not expected to be significant.

II. RESULTS AND DISCUSSION

A. Experiment

The polycrystalline samples Sm_2Co_{17} and Er_2Co_{17} were obtained by arc melting technique. High purity (99.99%) rare-earth and cobalt elements were melted in a water-cooled copper crucible under 5×10^{-1} torr argon pressure. In order to compensate the loss of samarium during melting a 5% excess with respect to the ideal composition was added. The ingots were remelted three times to insure homogeneity, then

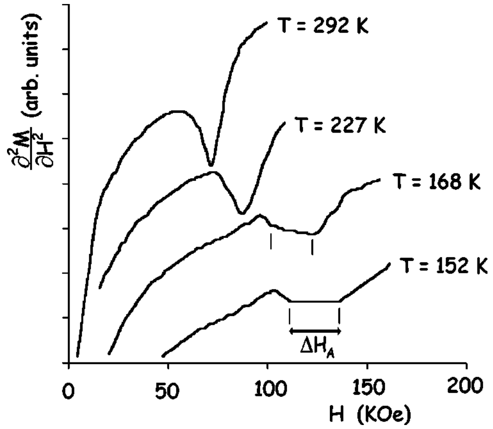

FIG. 1. SPD measurements of the anisotropy field of Sm_2Co_{17} at different temperatures. The SPD peak enlarges at lower temperatures, as is expected in presence of two different anisotropy fields.

wrapped in tantalium foil, annealed under argon atmosphere at 900 °C (7 days) and then quenched in water. Thermomagnetic analysis and x-ray diffraction showed the presence of rhomboedral 2:17 phase only. Singular point detection (SPD) measurements[12,13] of the anisotropy field were then performed at different temperatures (78 – 300 K). In order to enhance the SPD signal, grain oriented specimens were prepared by aligning in a magnetic field the powder grains dispersed in a resin.

The usual phenomenological approach to the problem of the magnetocrystalline anisotropy consists in writing the anisotropy energy as a sum of trigonometric functions of the angle θ between the magnetization direction and the easy magnetization axis (in our case the crystallographic c axis) and the azimuthal angle ϕ. For R_2Co_{17} the anisotropy free energy expression up to the sixth order is

$$E_A(\theta,\phi)=K_1\sin^2\theta+K_2\sin^4\theta+K_3\sin^6\theta+K_3'\sin^6\theta\cos 6\phi \tag{1}$$

which accounts for the overall (RE and Co) system anisotropy. The basal plane anisotropy free energy $E_A(\pi/2,\phi)$ is described by the sixth-order term and is a periodical function of ϕ (with a period of $\pi/3$), which has a maximum at $\phi=n(\pi/3)$ (assuming that $K_3'>0$) and a minimum at $\phi=(2n+1)(\pi/6)$, $n=0,1,\ldots,5$. From the total energy of the system in an applied magnetic field, given by $E=E_A(\theta,\phi)-\mathbf{H}\cdot\mathbf{M}_S$, the expression of the anisotropy field H_A, defined as the field value required to saturate $\mathbf{M}_S$ in a hard direction, can be derived. For the two directions in the basal plane (say x and y, defining the x axis as $\theta=\pi/2$, $\phi=0$) the anisotropy field is expressed by

$$H_A=\frac{2K_1+4K_2+6K_3\pm 6K_3'}{M_S}. \tag{2}$$

In the case of Sm_2Co_{17} the single sharp SPD peak detected at 293 K, which represents the anisotropy field when all the directions in the basal plane are equivalent (i.e., there is no in-plane anisotropy), broadens with decreasing temperature (Fig. 1) and develops into two peaks, as it should be if two different anisotropy fields are present. In this case the two detected values correspond to H_A along the two different hard directions in the basal plane (a, b), and they can be described by Eq. (2). The occurrence of two different values of H_A for saturating along a and b directions is also evident from the differences in the magnetization curves $M(H)$ of single crystal Sm_2Co_{17} (Ref. 10), even if the one along a is not brought to saturation.

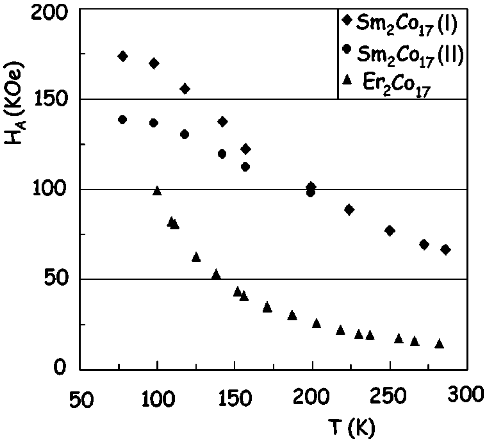

FIG. 2. Temperature dependence of the anisotropy field for Sm_2Co_{17} and Er_2Co_{17}. Two distinct values were detected for the former compound at temperatures lower than 200 K. The experimental values have been corrected for the demagnetizing field.

Thus knowledge of ΔH_A at a given temperature allows to determine the basal-plane anisotropy constant K_3' (which is only due to the Sm sublattice) by the simple relation

$$K_3'=\frac{\Delta H_A\cdot M_S}{12}. \tag{3}$$

The same measurements were performed on the isostructural compound Er_2Co_{17}. No basal-plane anisotropy was detected in the considered temperature range (100 – 293 K). It is worth noticing that we do not expect any relevant J-mixing effect for this compound, since the spin-orbit multiplets for Er^{3+} ion are well separated in energy. The experimental values of H_A for the two compounds are shown in Fig. 2.

B. Theory

Assuming the validity of a single-ion model with exchange and crystal field to account for the magnetocrystalline anisotropy of the Sm sublattice, the Hamiltonian is[4,14,15]

$$\hat{H}=\lambda\mathbf{L}\cdot\mathbf{S}+2\mu_B\mathbf{H}_{ex}\cdot\mathbf{S}+\hat{H}_{CF}. \tag{4}$$

In the ground-state multiplet the crystal-field term $\hat{H}_{CF}$ can be written by means of Stevens operator equivalents as

$$\hat{H}_{CF}=B_2^0\hat{O}_2^0+B_4^0\hat{O}_4^0+B_6^0\hat{O}_6^0+B_6^6\hat{O}_6^6, \tag{5}$$

where $B_K^Q=A_K^Q\langle r^K\rangle\Theta_K$ and Θ_K is the Kth-order Stevens factor (in the original notation, $\Theta_2\equiv\alpha$, $\Theta_4\equiv\beta$, $\Theta_6\equiv\gamma$). In this frame K_3' is directly proportional to the crystal-field parameter B_6^6 (Ref. 16):

$$K_3'(T)=\frac{1}{16}B_6^6\left(\langle\hat{O}_6^0\rangle+\frac{15}{2}\langle\hat{O}_6^2\rangle+3\langle\hat{O}_6^4\rangle+\frac{1}{2}\langle\hat{O}_6^6\rangle\right). \tag{6}$$

However, as the Stevens factor Θ_6 for the ground multiplet ($^6H_{5/2}$) of Sm^{3+} ion is zero, this description predicts absence of basal-plane anisotropy for Sm_2Co_{17} at all temperatures $[K_3'(T)\equiv 0]$. This is not consistent with the experimental data, which give a value of 3.2×10^6 erg/cm^3 for K_3' at 78 K. This fact may be attributed to the smallness of the gap between the two lowest Sm^{3+} energy multiplets. The strong exchange field in the ferromagnetic phase causes the spin-orbit multiplets of Sm^{3+} to mix heavily; this effect is neglected in Eq. (6), as the thermal average of Stevens operators $\langle \hat{O}_K^Q\rangle$ is taken over ground multiplet states only. Thus the contributions of excited multiplets (J mixing) has to be taken into account. To evaluate matrix elements between states with different J[2,11,14] the formalism of Racah's tensor operators must be used. The crystal-field Hamiltonian can be rewritten as

$$\hat{H}_{CF}=B_{20}\hat{C}_{20}+B_{40}\hat{C}_{40}+B_{60}\hat{C}_{60}+B_{66}(\hat{C}_{66}+\hat{C}_{6-6}), \quad (7)$$

where the crystal-field parameters B_{KQ} differ from the B_K^Q in Eq. (5) by constant coefficients and

$$C_{KQ}=\left(\frac{4\pi}{2K+1}\right)^{1/2}\sum_{i=1}^{n} Y_K^Q(\theta_i,\phi_i). \quad (8)$$

The partition function

$$Z=\mathrm{Tr}\exp\left(\frac{-\hat{H}}{k_BT}\right) \quad (9)$$

allows us to calculate the free energy $F=-k_BT\ln Z$ for each given set of parameters.

From Eq. (1) a simple way to express K_3' in terms of the anisotropy energy can be deduced:

$$E_A\left(\theta=\frac{\pi}{2},\phi=0\right)-E_A\left(\theta=\frac{\pi}{2},\phi=\frac{\pi}{2}\right)=2K_3'. \quad (10)$$

Notice that the direction $\phi=\pi/6$ in the basal plane is equivalent to the y ($\phi=\pi/2$) direction because of hexagonal symmetry. In the following the calculation will be carried out within the subspace consisting of the ground multiplet $^6H_{5/2}$ and the two lowest excited multiplets $^6H_{7/2}$ and $^6H_{9/2}$. The two Hamiltonians to be diagonalized are

$$\hat{H}^{(x)}=\lambda\mathbf{L}\cdot\mathbf{S}+2\mu_BH_{ex}S_x+\hat{H}_{CF} \quad (11)$$

and

$$\hat{H}^{(y)}=\lambda\mathbf{L}\cdot\mathbf{S}+2\mu_BH_{ex}S_y+\hat{H}_{CF}. \quad (12)$$

By rotating the reference frame in order to align the exchange field with the angular momentum quantization axis (z axis), Eqs. (11) and (12) become, respectively,

$$\{\hat{H}^{(x)}\}^{\theta=\pi/2}_{\phi=0}=\lambda\mathbf{L}\cdot\mathbf{S}+2\mu_BH_{ex}S_z+\{\hat{H}_{CF}\}^{\theta=\pi/2}_{\phi=0} \quad (13)$$

and

$$\{\hat{H}^{(y)}\}^{\theta=\pi/2}_{\phi=\pi/2}=\lambda\mathbf{L}\cdot\mathbf{S}+2\mu_BH_{ex}S_z+\{\hat{H}_{CF}\}^{\theta=\pi/2}_{\phi=\pi/2}. \quad (14)$$

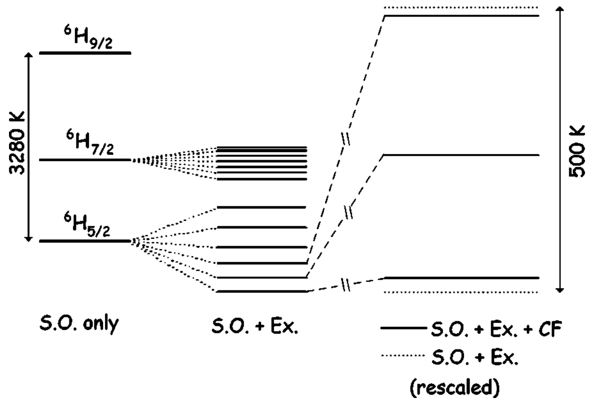

FIG. 3. Structure of energy levels of Sm^{3+} ion. The effect of RE-TM exchange interaction on the two lowest manifolds is shown. On the right side, the effect of crystal field on the three lowest eigenstates is shown. A different scale had to be used due to the smallness of the CF splittings.

The general rules for any rotation of tensor operators are well known.[17,18] It is worth noticing that the rotated Racah tensor operator $\{C_{KQ}\}$ depends on the angle ϕ through the factor $e^{iQ\phi}$ only. Therefore the total single-ion Hamiltonian can be written as

$$\hat{H}^{(x,y)}=\hat{H}_0\pm B_{66}\hat{H}' \quad (15)$$

with

$$\hat{H}_0=\lambda\mathbf{L}\cdot\mathbf{S}+2\mu_BH_{ex}S_z+B_{20}\{\hat{C}_{20}\}^{\theta=\pi/2}+B_{40}\{\hat{C}_{40}\}^{\theta=\pi/2}+B_{60}\{\hat{C}_{60}\}^{\theta=\pi/2} \quad (16)$$

and

$$\hat{H}'=\frac{\sqrt{231}}{16}\hat{C}_{60}+\frac{3\sqrt{55}}{32}(\hat{C}_{62}+\hat{C}_{6-2})+\frac{\sqrt{66}}{32}(\hat{C}_{64}+\hat{C}_{6-4})+\frac{1}{32}(\hat{C}_{66}+\hat{C}_{6-6}). \quad (17)$$

The plus sign in Eq. (15) corresponds to the x direction for the exchange field. The brackets and the rotation angles in the first member of Eq. (15) have been omitted for simplicity.

In the ferromagnetic phase the exchange interaction is much stronger than the crystal field, so the crystal-field parameter B_{66} does not affect significantly the energy levels (Fig. 3), although it will be crucial to account for the effect we are considering. Thus, knowing the eigenvalues (E_i^0) and eigenvectors ($|i\rangle$) of $\hat{H}_0$, first-order perturbation theory can be used to find the eigenvalues of $\hat{H}^{(x)}$ and $\hat{H}^{(y)}$ ($E_i^{(x)}$ and $E_i^{(y)}$, respectively):

$$E_i^{(x,y)}=E_i^0\pm B_{66}\langle i|\hat{H}'|i\rangle. \quad (18)$$

The internal energy of the system for each direction of the exchange field is

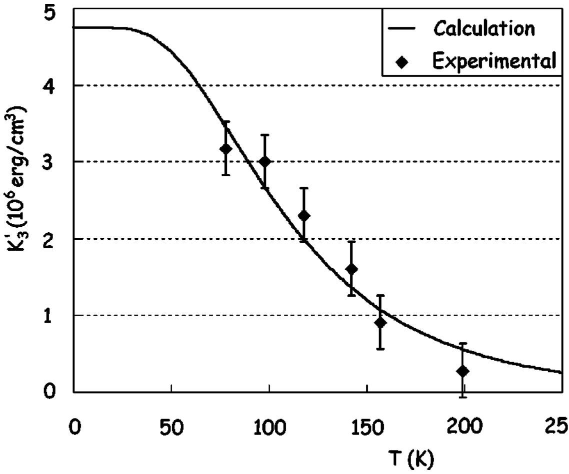

FIG. 4. Temperature dependence of the basal-plane anisotropy constant K'_3 for Sm_2Co_{17}.

$$U^{(x,y)}=\frac{\sum_i E_i^{(x,y)}\exp\left(-\frac{E_i^{(x,y)}}{k_BT}\right)}{\sum_i \exp\left(-\frac{E_i^{(x,y)}}{k_BT}\right)}$$

$$\approx\frac{\sum_i (E_i^0\pm B_{66}\langle i|\hat{H}'|i\rangle)\exp\left(-\frac{E_i^0}{k_BT}\right)}{\sum_i \exp\left(-\frac{E_i^0}{k_BT}\right)} \tag{19}$$

so that

$$\Delta U=U^{(x)}-U^{(y)}\approx B_{66}\frac{2\sum_i \langle i|\hat{H}'|i\rangle\exp\left(-\frac{E_i^0}{k_BT}\right)}{\sum_i \exp\left(-\frac{E_i^0}{k_BT}\right)}. \tag{20}$$

From this formula ($\Delta U\propto B_{66}$), it can be inferred that also the free energy difference between the two configurations is proportional to B_{66} ($\Delta F=\Delta U+T\Delta S$, with $\Delta S=\int_0^T(1/T')\times\{[\partial(\Delta U)]/\partial T'\}dT'$). It follows that

$$K'_3(T)\propto B_{66} \quad \text{(at all temperatures)} \tag{21}$$

which implies that a variation of the crystal-field parameter B_{66} does not modify the shape of the curve $K'_3(T)$, calculated by means of Eq. (10). In other words, B_{66} can be considered as a scaling factor: the same happens in absence of J mixing [see Eq. (6)]. The parameters λ, H_{ex}, B_{K0} ($K=2,4,6$) determine the unperturbed eigenvalues E_i^0: however, it is known that the exchange parameter is responsible for the main structure of energy levels, while the crystal field (and in particular the terms of order higher than the second) can be considered as a perturbation (Fig. 3). Thus, while even large variations of the crystal-field parameters B_{K0} should have little effect on the curve $K'_3(T)$, a change of the H_{ex} value can modify it strongly. For the above reasons B_{40} and B_{60} were neglected, while the literature values $\lambda=410$ K (Ref. 15), $2\mu_BH_{ex}=442$ K, and $B_{20}=-208$ K (Ref. 19) were used. A good fit of the experimental $K'_3(T)$ is obtained with $B_{66}=-410$ K (Fig. 4). As a result of our calculation, the basal-plane anisotropy constant at 0 K has a value of about 4.7×10^6 erg/cm^3. The composition of the lowest eigenstates of Sm^{3+} ion calculated with these parameters is reported in Table I.

All attempts to satisfactorily fit the experimental data in the considered temperature range using parameters significantly different from those proposed above were unsuccessful. In particular, the extension of the flat low-temperature zone is directly correlated to the energy splitting between the ground and the first excited state, which increases with the exchange field. In other words, increasing H_{ex} results in an enlargement of the temperature range in which $K'_3(T)\simeq K'_3(0)$.

Moreover, the SPD analysis of the isostructural Er_2Co_{17} compound (for which we do not expect a particular relevance of J-mixing effect) shows that $K'_3(T)$ is zero within the experimental uncertainty at temperatures higher than 100 K, even if the calculated value of $K'_3(0)$ for this compound is larger than for Sm_2Co_{17}.[9] In fact, as shown in Fig. 2, the value of the anisotropy field for Er_2Co_{17} drops more rapidly than for Sm_2Co_{17}. This can be explained assuming that the sixth-order anisotropy terms remain relevant at higher temperatures for the latter compound. This suggests that an effect of strong J mixing for intermetallic compounds of the R_2Co_{17} class may be a significant change in the temperature dependence of the anisotropy field.

III. CONCLUSIONS

The basal-plane anisotropy of Sm_2Co_{17} cannot be accounted for without considering the contributions of the excited J manifolds of Sm^{3+} ion. This confirms the importance of the J-mixing effect for Sm-Co intermetallic compounds. The measurement of the in-plane anisotropy field and the deduction of the sixth-order anisotropy constant K'_3 can be

TABLE I. The composition of the six lowest eigenstates is tabulated. Only states accounting for more than 0.25% of the total wave function are listed.

Energy (K)	Eigenstate composition
0.00	$-0.9793\|5/2,-5/2\rangle+0.1966\|7/2,-5/2\rangle$
216.79	$+0.9586\|5/2,-3/2\rangle-0.2766\|7/2,-3/2\rangle$
461.32	$-0.9377\|5/2,-1/2\rangle+0.3362\|7/2,-1/2\rangle-0.0590\|9/2,-1/2\rangle$
739.05	$-0.9182\|5/2,+1/2\rangle+0.3837\|7/2,+1/2\rangle-0.0745\|9/2,+1/2\rangle$
1060.46	$-0.9018\|5/2,+3/2\rangle+0.4196\|7/2,+3/2\rangle-0.0875\|9/2,+3/2\rangle$
1449.64	$-0.8958\|5/2,+5/2\rangle+0.4327\|7/2,+5/2\rangle-0.0936\|9/2,+5/2\rangle$

considered as a direct evidence of the strength of J-mixing effect in this compound and it offers a good way to estimate the sixth-order CF parameter B_{66}. In fact it has been shown, with good approximation, that K_3' and B_{66} are proportional at all temperatures even in case of J mixing of the lowest multiplets.

From a comparison of the anisotropy of Sm_2Co_{17} and Er_2Co_{17} it appears that an effect of J mixing might be the smoothing of the temperature decrease of $K_3'(T)$. This hypothesis should be verified by measuring and analyzing the temperature dependence of the basal-plane anisotropy constant for the whole 2:17 class of compounds.

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