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CRYSTAL–FIELD ANISOTROPY OF Sm^{3+} IN $SmCo_5$

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It is shown that the major contribution to the high uniaxial anisotropy of the compound $SmCo_5$ arises from the action of crystalline and exchange fields on the Sm^{3+} ion.

IN THE series of trivalent rare-earth ions, Sm^{3+} is unique in the sense that the energy separation between the ground $J = 5/2$ multiplet and the first excited multiplet is only 1400 K, while in addition the ground multiplet has a small g-value. The presence of crystalline and/or exchange fields will in general lead to a considerable mixing of the higher multiplets into the ground state which in systems containing Sm^{3+} ions may have its impact on a variety of physical properties, such as the temperature dependence of the Knight shift and the magnetic susceptibility, the saturation moment and direction of the easy axis in magnetically ordered compounds, the sign of the conduction electron spin polarization, and the neutron magnetic form factor, All these aspects have been treated extensively in previous papers.[1–4] In the present study, we report calculations on the magnetocrystalline anisotropy of Sm^{3+} in $SmCo_5$, for which an extremely high uniaxial magnetocrystalline anisotropy has been observed.

We first review the experimental data that have become available from magnetic measurements on single crystals of $SmCo_5$ and the isomorphous RCo_5 compounds. It was found that the magnetocrystalline anisotropy for the compounds RCo_5 with R = La, Ce, Sm, Gd and Y is uniaxial in character with the preferred direction parallel to the hexagonal axis.[5] The angular dependence of the free energy for the present case of a hexagonal crystal structure may generally be written as

$$F = K_1 \sin^2\theta + K_2 \sin^4\theta + K_3 \sin^6\theta + K_4 \sin^6\theta \cos^6\varphi, \quad (1)$$

where the θ and φ represent the polar angles of the preferred direction of the magnetization relative to the crystal axes. It appeared, however, that at any temperature the experimental results for the anisotropy could well be described by K_1 alone, with neglect of the higher-order anisotropy constants. We will therefore truncate equation (1) to $F = K_1 \sin^2\theta$ in the further discussion. The experimental data for K_1 as a function of the temperature, as taken from the literature,[6,7] are reproduced in Fig. 1. The anisotropy in the compounds $LaCo_5$, YCo_5 and $CeCo_5$ is seen to be roughly equal. In these compounds, there is no $4f$ contribution to the anisotropy, so that K_1 reflects the strength of the anisotropy due to the cobalt sublattice alone.

In the presence of $4f$ electrons, one expects additional contributions to the anisotropy. One of these is of dipolar origin and is associated with the magnetic moment of the $4f$ electrons. If the rare-earth ion in RCo_5 has a non-zero orbital momentum, a second contribution arises from crystalline electric fields.

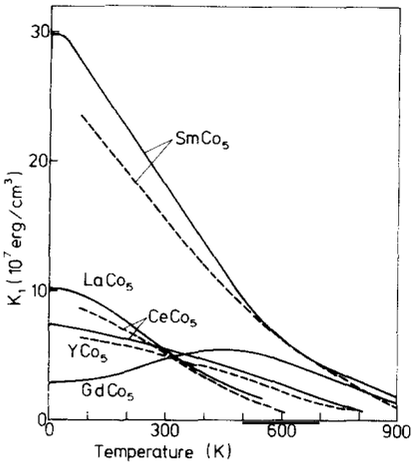

FIG. 1. Experimental values of the uniaxial anisotropy constant K_1 as a function of temperature for $SmCo_5$, $LaCo_5$, $CeCo_5$, YCo_5 and $GdCo_5$. The drawn curves represent data obtained with applied fields up to 83 kOe (reference 6), while the dashed curves are data obtained with applied fields up to 16 kOe (reference 7).

Since the Gd^{3+} ion has no orbital momentum, the first of these contributions can be estimated from the experimental data of $GdCo_5$. Comparison of the K_1 values of $GdCo_5$ with, for instance, YCo_5 shows that the dipolar contribution of the Gd sublattice is of the same magnitude as the contribution due to the Co atoms. The dipolar contribution in fact reduces K_1 below, say, 500 K, where the Gd sublattice is ordered appreciably. In view of the small magnetic moment of the Sm^{3+} ion ($\mu_{Sm} \leqslant 0.7\mu_B$) as compared to $7\mu_B$ of the Gd^{3+}, one is justified to neglect the dipolar contribution entirely in $SmCo_5$. For the explanation of the huge anisotropy in $SmCo_5$, we are therefore left with the single-ion anisotropy due to the action of crystalline fields on the Sm^{3+} ion. In concord with this view is the fact that in the series of RCo_5 compounds there is a one-to-one correspondence between the direction of easy magnetization and the sign of the second-order crystal field splitting.[8]

It will now be investigated whether the crystaline field induced single-ion anisotropy of Sm^{3+} is indeed able to account quantitatively for the observed K_1 of $SmCo_5$ and its temperature dependence. The energy levels of the Sm^{3+} ions in the presence of crystal fields and exchange fields are determined by the Hamiltonian

$$\mathcal{H} = \lambda \mathbf{L}\cdot\mathbf{S} + \mathcal{H}_c + 2\mu_B \mathbf{H}_{ex}\cdot\mathbf{S} \qquad (2)$$

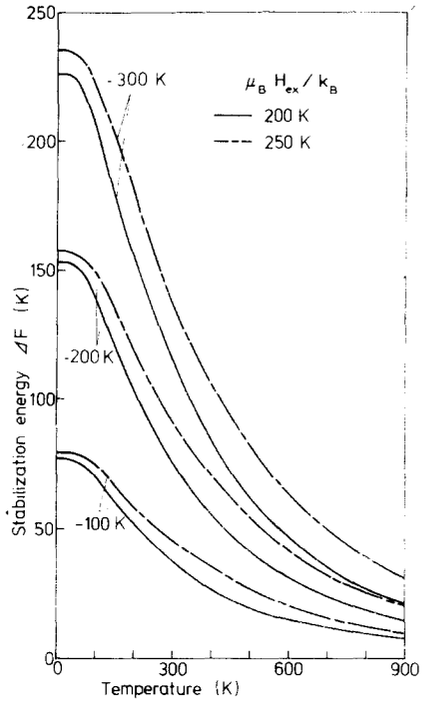

FIG. 2. Dependence of the stabilization energy ΔF on $A_2^0\langle r^2\rangle$ and H_{ex}, with $A_4^0\langle r^4\rangle$ and $A_6^0\langle r^6\rangle$ being kept zero.

In the first term, representing the spin–orbit coupling, we used $\lambda/k_B = 410$ K. The exchange field H_{ex} exerted on the Sm^{3+} by the surrounding Sm and Co ions was taken to be directed parallel to the crystallographic c-axis, or along the a or b axis in the basal plane. The crystal field Hamiltonian is given by

$$\mathcal{H}_c = A_2^0 \sum_i f_{20}(\mathbf{r}_i) + A_4^0 \sum_i f_{40}(\mathbf{r}_i) + A_6^0 \sum_i f_{60}(\mathbf{r}_i) + + A_6^6 \sum_i f_{66}(\mathbf{r}_i), \qquad (3)$$

where $f_{kq}(\mathbf{r})$ are linear combinations of the spherical harmonics $r^k Y_k^{\pm q}(\theta,\varphi)$. The calculation of the matrix elements of the fourth- and sixth-order potentials was already described in a previous paper.[1] In calculating the second-order potentials the same procedure was followed, but with the reduced matrix element

$$\langle L \| \Sigma_i r^2 Y_2 \| L\rangle = c_{20}\langle r^2\rangle \times (2^3 \times 3^{-3} \times 5^{-1} \times 11 \times 13)^{\frac{1}{2}}.$$

Using various values for the crystal field parameters $A_2^0\langle r^2\rangle$, $A_4^0\langle r^4\rangle$, $A_6^0\langle r^6\rangle$, $A_6^6\langle r^6\rangle$, and the exchange

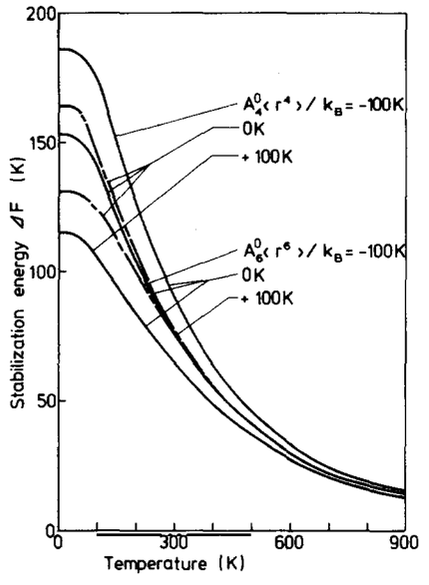

FIG. 3. Dependence of the stabilization energy ΔF on $A_4^0\langle r^4\rangle$ and $A_6^0\langle r^6\rangle$, with $A_2^0\langle r^2\rangle/k_B = 200$ K and $\mu_B H_{ex}/k_B = 200$ K.

field H_{ex}, we have calculated the energy levels of Sm^{3+} by diagonalizing equation (2) for the lowest three multiplets $J = 5/2$, $7/2$, and $9/2$. These levels have subsequently been used to calculate the partition function Z and the Helmholtz free energy $F = -k_B T \ln Z$. The stabilisation energy ΔF of a moment alignment parallel to the c-axis relative to an alignment in the basal plane (a or b direction) is now obtained by subtraction of the corresponding free energies.

As far as anisotropy in the basal plane is concerned, for which $A_6^6\langle r^6\rangle$ is responsible, it was found that, even if $A_6^6\langle r^6\rangle$ is of the same order of magnitude as $A_2^0\langle r^2\rangle$, basal plane anisotropy amounts to only a few percent of the axial anisotropy. Also experimentally basal plane anisotropy could not be detected.[7] In the following we will therefore not consider $A_6^6\langle r^6\rangle$ any further.

The relative influence of the remaining parameters, $A_2^0\langle r^2\rangle$, $A_4^0\langle r^4\rangle$, $A_6^0\langle r^6\rangle$ and H_{ex} is visualized in Figs. 1, 2 and 3. In Fig. 2 we have kept $A_4^0\langle r^4\rangle$ and $A_6^0\langle r^6\rangle$ equal to zero, and have varied $A_2^0\langle r^2\rangle$, which was found to give rise to the largest contribution to ΔF, and H_{ex}. It appears that H_{ex} has a very small influence on ΔF at zero temperature, but is of considerable importance on the temperature dependence of ΔF. The smaller the exchange field the more rapidly ΔF falls off with the temperature. In Fig. 3 we have kept $A_2^0\langle r^2\rangle$ and

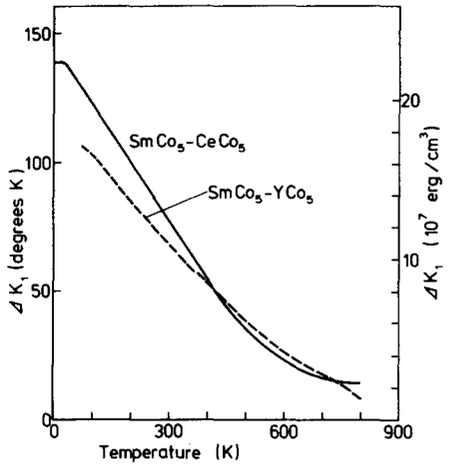

FIG. 4. The effect on K_1 from the Sm^{3+} ions alone as a function of temperature. The drawn curve is derived from reference 6 as the difference between the anisotropies of $SmCo_5$ and $CeCo_5$. The dashed curve is the difference between $SmCo_5$ and YCo_5 as derived from reference 7.

H_{ex} constant, and varied $A_4^0\langle r^4\rangle$ and $A_6^0\langle r^6\rangle$. Inspection of this figure shows that $A_6^0\langle r^6\rangle$ has only a small effect on ΔF while the fourth-order potential term can contribute significantly to ΔF. It is finally noted that mixing of $J = 7/2$ and higher multiplets into $J = 5/2$ accounts for about one third of the calculated anisotropy.

A comment should be made on the validity of the calculational method, since the experimental K_1 represents the development of the free energy for small angular deviations of the magnetization, rather than a 90° turn from the easy axis to the basal plane. Even in a field of 100 kG, the Co moments will not be pulled from the easy axis by more than 10° at helium temperatures. We have therefore compared the present method with a more elaborate calculation, in which K_1 was determined from the angular dependence of the free energy near $\theta = 0°$. For a typical case, $A_2^0\langle r^2\rangle/k_B = -180$ K, $\mu_B H_{ex}/k_B = 200$ K, and the other parameters zero, we find that the present method overestimates K_1 by about 20 per cent at $T = 0$ K, falling to 3 per cent at 500 K. In the following we will identify the stabilization energy ΔF with K_1, but note in passing that the actual $A_2^0\langle r^2\rangle/k_B$ may be somewhat larger in absolute value and H_{ex} somewhat smaller than those obtained from comparison with the experimental data.

We will now compare the computational results with the experimental data. In order to make such a

comparison we first have to subtract the contribution of the Co sublattice anisotropy from the $SmCo_5$ data. This can be done by using the data of YCo_5 or $CeCo_5$. The $K_1(T)$ curve obtained for $SmCo_5$ in this way is plotted in Fig. 4. If this curve is compared with the results of the calculations, represented in part in Figs. 2 and 3, it is found that the observed magnitude and temperature dependence of K_1 can be fitted satisfactorily by $A_2^0\langle r^2\rangle/k_B \approx -180$ K, $\mu_B H_{ex}/k_B \approx 200$ K, with $A_4^0\langle r^4\rangle$ and $A_6^0\langle r^4\rangle$ small. However, since the effects of fourth-order and sixth-order crystal fields on the shape of the calculated curves are relatively minor, their existence cannot be excluded or confirmed. In particular, a fourth-order field would have some bearing on the $A_2^0\langle r^2\rangle$ required to fit the experiment, but $A_2^0\langle r^2\rangle$ is not expected to vary by more than, say, 50 K.

The magnitude of H_{ex}, acting on the Sm spin, may be estimated from other experiments. This exchange field is composed of a contribution from the Sm–Sm exchange and a contribution from the Sm–Co exchange. The first contribution can be estimated from the asymptotic Curie temperatures available for the series RNi_5, in which Ni does not have a magnetic moment,[9] to be a few degrees Kelvin only. An impression of the Sm–Co interaction can be obtained by comparison with the Tb–Co interaction in $TbCo_5$, for which compound neutron diffraction data are available. The Co-sublattice magnetization as well as the Tb sublattice magnetization have separately been determined[10] as a function of the temperature in the region 4.2–450 K. The Co moments appear to be almost constant in this range, so that the exchange field exerted on the Tb ions by the Co moments can also be regarded as constant. An estimate of H_{ex} is then obtained by comparing the experimental data of the Tb moments with

$$M = NgJ\mu_B B_J\left(\frac{2\mu_B H_{ex}(g-1)J}{k_B T}\right), \qquad (4)$$

where $B_J(x)$ is the Brillouin function. For the Tb^{3+} ion in $TbCo_5$ we find a value of $\mu_B H_{ex}/k_B = 180 \pm 60$ K from this procedure, of the right order of magnitude to account for the observed temperature dependence of K_1 in $SmCo_5$.

In conclusion it can be said that the large uniaxial anisotropy observed for $SmCo_5$ as well as its temperature dependence can adequately be explained in terms of the single-ion anisotropy of the Sm^{3+} ion. This anisotropy essentially arises through the combined action of crystalline fields and exchange fields, and involves a mixing of excited multiplet levels into the ground $J = 5/2$ level.

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Es wird gezeigt, dass der Hauptbeitrag der hohen uniaxialen Anisotropie der Verbindung $SmCo_5$ auf die Wirkung von Kristallfeldern und Exchangefeldern auf das Sm^{3+}-Ion zurückzuführen ist.