

# Determination of crystal-field parameters of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ and $\text{Sm}_2\text{Fe}_{17}\text{C}_3$

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**Abstract**—The crystal-field parameters  $A_{20}$  and  $A_{40}$  were determined from the magnetocrystalline anisotropy constants  $K_1$  and  $K_2$  in a linear approximation for  $\text{Sm}_2\text{Fe}_{17}\text{Z}_x$  ( $Z = \text{N}, \text{C}$ ) compounds. For the materials investigated, the values of  $K_1$  and  $K_2$  in a temperature range from 4.2 – 533 K have been obtained by a fit of demagnetization curves. The parameters  $A_{n0}$  are calculated in two ways: i) from the  $K_i$  at zero temperature and ii) from the temperature dependence of the  $K_i$ . Both methods give equivalent results. The value  $A_{20} \approx -400 \text{ Ka}_0^{-2}$  has been obtained which corresponds to an inverse THOMAS-FERMI screening length  $q \approx 2.3 \text{ \AA}^{-1}$  calculated within the framework of the screened charge model.

## I. INTRODUCTION

Interstitial modification of  $\text{RE}_2\text{Fe}_{17}$  (RE – rare-earth) strongly modifies the magnetocrystalline anisotropy and the Curie temperature of the parent material. In the most interesting case of rhombohedral  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  [1], a Curie temperature of 476°C and an anisotropy field  $\mu_0 H_A \approx 21 \text{ T}$  with easy axis type anisotropy is achieved. The drastic change of the magnetocrystalline anisotropy is due to the crystalline electric field (CEF) of the interstitial atoms (N, C, or/and H) acting on the aspherical 4f shell of the RE. This anisotropy is transferred to the 3d electron system via strong Fe-RE coupling. Neglecting in-plane anisotropy for uniaxial structures, the density  $f_a$  of the magnetocrystalline anisotropy energy can be described by a series expansion in the cosine of  $\vartheta$ , the angle of the magnetization with respect to the crystallographic c-axis. Up to third order this results in

$$f_a = K_1 \sin^2 \vartheta + K_2 \sin^4 \vartheta + K_3 \sin^6 \vartheta . \quad (1)$$

In this investigation, we determine the CEF parameters  $A_{n0}$  from the temperature dependence of anisotropy constants  $K_i(T)$ . A fit of the demagnetization curves [2] has provided the values of  $K_i$ , the spontaneous polarization

$J_s$ , as well as a texture parameter describing the grain alignment inside the polycrystalline samples.

## II. MODELS

The strong exchange coupling of the Fe 3d electrons gives rise to the ferromagnetic behaviour of the intermetallic compounds and  $J_s$  is mainly determined by these electrons. However, the magnetocrystalline anisotropy originates from the RE 4f electrons and is transferred via 4f-5d exchange coupling and 5d-3d hybridization to the 3d electrons of the iron and hence to the spontaneous polarization.

In order to calculate the CEF parameters from the anisotropy constants the Hamiltonian of a single RE-ion is considered

$$\mathcal{H} = \mathcal{H}_{so} + \mathcal{H}_{ex} + \mathcal{H}_{CEF} + \mathcal{H}_H , \quad (2)$$

where  $\mathcal{H}_{so}$  describes the spin-orbit interaction,  $\mathcal{H}_{ex}$  the Fe-RE exchange interaction,  $\mathcal{H}_{CEF}$  the interaction due to the CEF and  $\mathcal{H}_H$  the energy contribution by an applied field, respectively. In the REs of interest here, the spin-orbit interaction is considerably larger than the other energy contributions, resulting in the total angular momentum  $\mathcal{J}$  being a good quantum number. Here, the considerations are restricted to the ground state of  $\mathcal{H}_{so}$ , only (higher  $\mathcal{J}$  states are ignored) and  $\mathcal{J}$  is determined according to HUND's rules. In the case of Sm where admixed  $\mathcal{J}$  multiplets have to be taken into account [3], [4] this restriction may result in inaccuracies of the parameters to be determined. But according to [5] this inaccuracy is expected to be small since  $\mathcal{J}$ -mixing and non-linear effects have opposite influence on  $A_{20}$ . In order to describe the Fe-RE exchange interaction usually an exchange field  $\vec{B}_{ex}$

$$\mathcal{H}_{ex} = 2(g_{\mathcal{J}} - 1)\mu_B \vec{B}_{ex} \hat{\mathcal{J}} \quad (3)$$

( $g_{\mathcal{J}}$  – LANDÉ factor,  $\mu_B$  – BOHR magneton) is introduced, which is estimated in a mean field approximation. For the RE intermetallics under consideration the exchange between the Sm-ions [6] as well as the contribution of the RE-ion to the spontaneous polarization [7] can be neglected and hence,  $\vec{B}_{ex} = n_{FeRE} \vec{J}_s(T)$ , where  $n_{FeRE}$  is the molecular field coefficient. The moments of Fe sites are described by the net magnetization  $J_s(T)$ .

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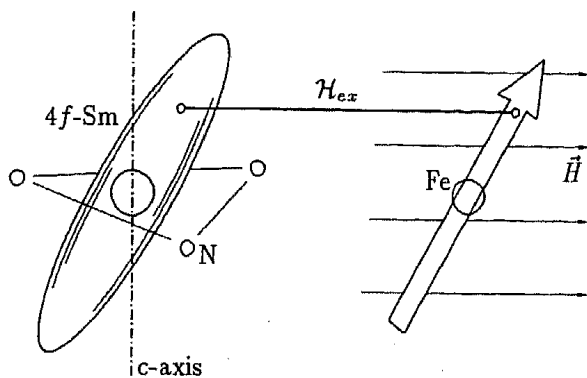


Fig. 1. Illustration of the origin of the magnetocrystalline anisotropy in the interstitially modified  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  compound. The alignment of the RE 4f electrons due to the CEF in the crystal lattice is transferred by exchange coupling to the Fe 3d electrons.

The operator of the CEF interaction is expressed by its projection onto the  $\mathcal{J}$  multiplet of the RE. With that, (2) can be rewritten

$$\mathcal{H} = 2(g_{\mathcal{J}} - 1)\mu_B \vec{J} n_{FeRE} \vec{J}_s(T) + \sum \theta_n A_{nm} \langle r^n \rangle \hat{O}_n^m \quad (4)$$

where the influence of  $\mathcal{H}_H$  is taken into account via the direction of  $\vec{J}_s(T)$ . The Stevens operators  $\hat{O}_n^m$ , the Stevens coefficients  $\theta_n$  and the averaged  $n$ -th power of the 4f radius,  $\langle r^n \rangle$ , refer to the  $\text{RE}^{3+}$  ion [8], [9], whereas the CEF (expressed by  $A_{nm}$ ) is mainly due to the interstitial atoms. In the rhombohedral  $\text{Th}_2\text{Zn}_{17}$  and the hexagonal  $\text{Th}_2\text{Ni}_{17}$ , three interstitial atoms (in case of complete interstitial modification) located at the 9e and the 6h sites, respectively, surround the RE-ions in a plane perpendicular to the crystallographic  $c$ -axis (Fig. 1, case of  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ ). In general, for one RE ion in the structures considered  $A_{20}$ ,  $A_{40}$ ,  $A_{43}$ ,  $A_{60}$ ,  $A_{63}$  and  $A_{66}$  have to be taken into account. In-plane anisotropy is neglected (cf. (1)). Comparing the angular dependences of the energy following from (4) with (1) within a linear approximation [10] results in

$$\begin{aligned} K_1 &= -\frac{3}{2}\kappa_{20} - 5\kappa_{40} - \frac{21}{2}\kappa_{60} + K_1^{Fe} \\ K_2 &= \frac{35}{8}\kappa_{40} + \frac{189}{8}\kappa_{60} \\ K_3 &= -\frac{231}{16}\kappa_{60}, \end{aligned} \quad (5)$$

where the anisotropy coefficients are given by

$$\kappa_{n0} = N_{RE} \theta_n A_{n0} \langle r^n \rangle \langle O_n^0 \rangle_T \quad (6)$$

Here,  $N_{RE}$  is the density of the  $\text{RE}^{3+}$  ions and  $K_1^{Fe}$  is the 3d anisotropy contribution.

The thermal averages  $\langle O_n^m \rangle_T$  of the operators equivalent can be calculated in different ways depending on the temperature considered:

i) A convenient way is to consider zero temperature [11] where  $\mathcal{J}_z = \mathcal{J}$  and hence [8]

$$\begin{aligned} \langle O_2^0 \rangle_{T=0} &= 3\mathcal{J}_z^2 - (\mathcal{J} + 1)\mathcal{J} = 2\mathcal{J}^2 - \mathcal{J} \\ \langle O_4^0 \rangle_{T=0} &= 8\mathcal{J}^4 - 24\mathcal{J}^3 + 22\mathcal{J}^2 - 6\mathcal{J} \\ \langle O_6^0 \rangle_{T=0} &= 16\mathcal{J}^6 - 120\mathcal{J}^5 + 340\mathcal{J}^4 - 450\mathcal{J}^3 + 274\mathcal{J}^2 - 60\mathcal{J}. \end{aligned} \quad (7)$$

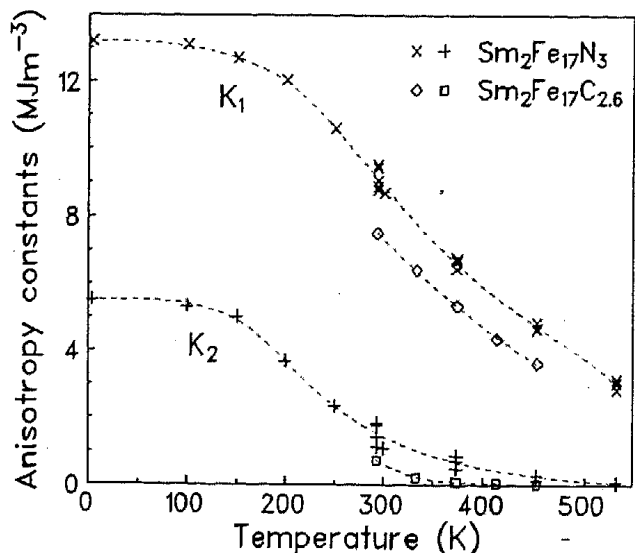


Fig. 2. Temperature dependences of the anisotropy constants  $K_1$  and  $K_2$  determined experimentally from several  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  and  $\text{Sm}_2\text{Fe}_{17}\text{C}_{2.6}$  samples.

However, the determination of the anisotropy constants which may attain high values at very low temperature (cf. Fig. 2) requires special effort in the measurement of the corresponding demagnetization curves.

ii) For arbitrary temperature,  $\langle O_n^m \rangle_T$  can be expressed [10] by the generalized BRILLOUIN functions  $B_{\mathcal{J}}^{(n)}(x)$

$$\begin{aligned} \langle O_2^0 \rangle_T &= 2\mathcal{J}^2 B_{\mathcal{J}}^{(2)}(x) \\ \langle O_4^0 \rangle_T &= 8\mathcal{J}^4 B_{\mathcal{J}}^{(4)}(x) \\ \langle O_6^0 \rangle_T &= 16\mathcal{J}^6 B_{\mathcal{J}}^{(6)}(x). \end{aligned} \quad (8)$$

Here, the argument  $x = 2\mathcal{J} |g_{\mathcal{J}} - 1| \mu_B n_{FeRE} J_s / k_B T$  is given by the ratio of exchange and thermal energy. Hence, for the determination of the  $A_{nm}$  the temperature dependences of  $K_1(T)$ ,  $K_2(T)$  ... and  $J_s(T)$  are employed. It should be noted that this approach incorporates more information than the determination of the  $A_{n0}$  from one curve  $H_A(T)$  only as performed in [3], [4], [7].

The equivalence of both considerations (cf. (7) and (8)) can be easily shown by calculation of the zero temperature limit of the BRILLOUIN functions, e.g.

$$\mathcal{J}^2 B_{\mathcal{J}}^{(2)}(T \rightarrow 0) = \mathcal{J}^2 \left( 1 - \frac{1}{2\mathcal{J}} \right). \quad (9)$$

### III. RESULTS

The anisotropy constants  $K_1$ ,  $K_2$  and the spontaneous polarization  $J_s$  of  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  have been determined by fitting demagnetization curves measured at various temperatures. In the case of RE = Sm, the ground state is given by  $\mathcal{J} = \frac{5}{2}$  and hence,  $A_{60}$  and correspondingly  $K_3$  vanish. The temperature dependence of  $K_1$  and  $K_2$  is shown in Fig. 2. Note the large number of investigated samples and the broad temperature region. The 3d anisotropy contribution was determined from  $K_1^{Fe}$  of  $\text{Y}_2\text{Fe}_{17}\text{N}_3$  scaled with respect to the Curie temperature.

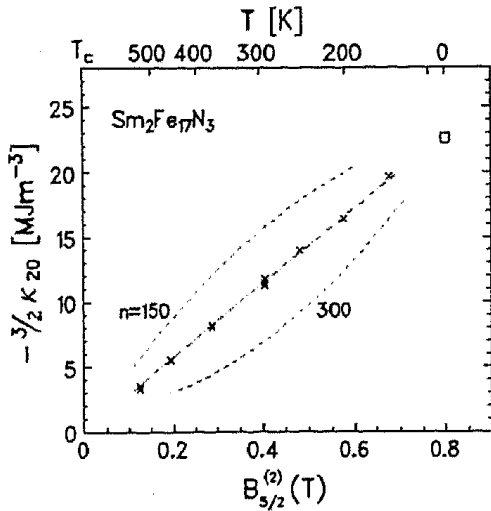


Fig. 3. Anisotropy coefficient  $-\frac{3}{2}\kappa_{20}$  deduced from measured  $K_1$  and  $K_2$  versus the temperature-dependent value of the Brillouin function for different molecular field coefficients  $n_{FeSm}$ . Results for  $T = 4.2$  K correspond to  $B_{5/2}^{(2)}(T \rightarrow 0) = 0.8$ .

From the  $K_i$  measured at 4.2 K the CEF parameters can be calculated from (5), (6) and (7). Values  $A_{20} = -386 \text{ Ka}_0^{-2}$  and  $A_{40} = 39 \text{ Ka}_0^{-4}$  have been obtained.

For arbitrary temperature, the argument  $x$  depends on  $n_{FeRE}$ , too. However, in a plot of  $\kappa_{n0}$  versus  $B_{\mathcal{J}}^{(n)}(x)$  its value determines the curvature of the line connecting the measured points. In Fig. 3 the example  $\kappa_{20}$  vs.  $B_{5/2}^{(2)}$  for  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  is shown. From the linear dependence expected from (6) and (8), the value of  $n_{FeRE}$  can be estimated. From Fig. 3,  $n_{FeSm} \approx 210$  in good agreement with the results obtained from  $T_c$  analysis ( $n_{FeSm} \approx 260$ ). The CEF parameters can be determined from the slope of the curves corresponding to (6). Values  $A_{20} = -410 \text{ Ka}_0^{-2}$  and  $A_{40} = 72 \text{ Ka}_0^{-4}$  are obtained. For comparison, the result obtained at 4.2 K ( $B_{5/2}^{(2)}(T \rightarrow 0) = 0.8$ ) is included in Fig. 3, too. Note that the differences in the results presented above are mainly caused by the inaccuracies of the  $K_2$  data. The dependence of  $A_{20}$  on the nitrogen concentration  $c$  in  $\text{RE}_2\text{Fe}_{17}\text{N}_{3c}$  compounds can be analyzed by  $A_{20}(c) = A_{20}(0) + \frac{1}{2}c\xi A_2^Z$ , where  $\xi$  is the number of interstitial next neighbours [12] and  $Z$  is N or C.  $A_{20}(0) = 34 \text{ Ka}_0^{-2}$  from the Y compound. With this, the mean value per N atom,  $A_2^N \approx -290 \text{ Ka}_0^{-2}$  is obtained.

Results for  $\text{Sm}_2\text{Fe}_{17}\text{C}_{2.6}$  are  $A_{20} = -310 \text{ Ka}_0^{-2}$  and  $A_{40} = 66 \text{ Ka}_0^{-4}$ . Hence, a value  $A_2^C \approx -265 \text{ Ka}_0^{-2}$  has been found which is slightly lower (absolute value) than  $A_2^N$ . In case of the carbide,  $n_{FeSm} \approx 185$  has been obtained. Its slightly decreased value reflects the lower Curie temperature of the carbides compared to the nitrides.

Rather than the point-charge model [3], an improved analytical approach to calculate the CEF parameters in RE intermetallics is the screened-charge model [12]. Therein, the screening conduction electrons are considered as a weakly disturbed free-electron gas with inverse THOMAS-FERMI screening length  $q$ , whereas all non-4f charges of the RE are assumed to be well localized. As

the main result

$$A_2^Z = -\frac{eQ_{cf}}{4\pi\epsilon_0} \frac{e^{-qR}}{2R^3} \left(1 + qR + \frac{1}{3}q^2R^2\right), \quad (10)$$

where  $R$  is the distance between the RE and the ligand (e.g.  $R = 2.52 \text{ \AA}$  in  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ ). The calculation of the crystal field charges  $Q_{cf}$  is discussed in [12]. With the value of  $A_2^N$  for the Sm-nitride given above we obtain  $q \approx 2.3 \text{ \AA}^{-1}$ . This result is in agreement with  $q = 2 \text{ \AA}^{-1}$  for iron and  $q = 2.5 \text{ \AA}^{-1}$  for iron-rich RE intermetallics. The model was not applied to the carbides because in that case a stronger hybridization is expected.

For  $\text{Dy}_2\text{Fe}_{17}\text{N}_3$  ( $\mathcal{J} = \frac{15}{2}$ ) only a crude estimation for  $A_{20} = -170(\pm 60) \text{ Ka}_0^{-2}$  is obtained since determination of CEF parameters in RE compounds with  $\mathcal{J} > \frac{5}{2}$  is much more complicated: i)  $A_{60} \neq 0$  and hence  $K_3$  had to be determined from the data what turned out to be difficult. ii) In comparison to the Sm compound, the argument of the BRILLOUIN function is shifted to lower values where it is more sensitive to inaccuracies of the involved properties which have been measured. However, no  $\mathcal{J}$ -mixing is expected for Dy. Hence, the agreement of the  $A_{20}$ , which should not much vary for different REs, in their order of magnitude, can be considered as a fair result.

#### IV. CONCLUSION

CEF parameters were determined from the anisotropy constants. The agreement of the calculated CEF parameters for different samples and for two different temperature regions shows the reliability of the method. However, as discussed in [5] the parameters obtained here should be considered as effective CEF parameters since  $\mathcal{J}$ -mixing and nonlinear effects have been neglected.

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