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Determination of crystal-field parameters of $Sm_2Fe_{17}N_3$ and $Sm_2Fe_{17}C_3$

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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 $\text{Sm}_2\text{Fe}_{17}Z_x$ (Z = N, 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 $q \approx 2.3 \text{ Å}^{-1}$ calculated within the framework of the screened charge model.

I. INTRODUCTION

Interstitial modification of RE_2Fe_{17} (RE - rare-earth) strongly modifies the magnetocrystalline anisotropy and the Curie temperature of the parent material. In the most interesting case of rhombohedral Sm₂Fe₁₇N₃ [1], a Curie temperature of 476°C and an anisotropy field $\mu_0 H_A \approx 21$ 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 inplane anisotropy for uniaxial structures, the density f_a of the magnetocrystalline anisotropy energy can be described by a series expansion in the cosine of ϑ , the angle of the magnetization with respect to the crystallographic c-axis. Up to third order this results in

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

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

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

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 B_{ex}

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

 $(g_{\mathcal{J}} - \text{LANDÉ} \text{ factor}, \mu_B - \text{BOHR magneton})$ 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 $Sm_2Fe_{17}N_3$ 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

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

where the influence of \mathcal{H}_H is taken into account via the direction of $J_s(T)$. The Stevens operators \hat{O}_n^m , the Stevens coefficients θ_n and the averaged n-th power of the 4f radius, $\langle r^n \rangle$, refer to the RE³⁺ ion [8], [9], whereas the CEF (expressed by A_{nm}) is mainly due to the interstitial atoms. In the rhombohedral Th_2Zn_{17} and the hexagonal Th_2Ni_{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 $Sm_2Fe_{17}N_3$). 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

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

where the anisotropy coefficients are given by

$$\kappa_{n0} = N_{RE} \,\theta_n \,A_{n0} \langle r^n \rangle \langle O_n^0 \rangle_T \,. \tag{6}$$

Here, N_{RE} is the density of the RE³⁺ 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]



Fig. 2. Temperature dependences of the anisotropy constants K_1 and K_2 determined experimentally from several $Sm_2Fe_{17}N_3$ and $Sm_2Fe_{17}C_3$ 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 $B_T^{(n)}(x)$

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 $K_1(T), K_2(T) \dots$ 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.

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

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 3*d* anisotropy contribution was determined from K_1^{Fe} of $Y_2\text{Fe}_{17}\text{N}_3$ 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 $B_{5/2}^{(2)}(T \to 0) = 0.8$.

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 κ_{n0} versus $B_{\mathcal{T}}^{(n)}(x)$ its value determines the curvature of the line connecting the measured points. In Fig. 3 the example κ_{20} vs. $B_{5/2}^{(2)}$ for Sm₂Fe₁₇N₃ 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 RE₂Fe₁₇N_{3c} compounds can be analyzed by $A_{20}(c) = A_{20}(0) + \frac{1}{2}c\xi A_2^Z$, where ξ is the number of interstitial next neighbours [12] and Z is N or C. $A_{20}(0) = 34$ ${\rm Ka_0^{-2}}$ from the Y compound. With this, the mean value per N atom, $A_2^N \approx -290 {\rm Ka_0^{-2}}$ 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-4fcharges of the RE are assumed to be well localized. As

the main result

$$A_2^Z = -\frac{eQ_{cf}}{4\pi\varepsilon_0} \frac{e^{-qR}}{2R^3} \left(1 + qR + \frac{1}{3}q^2R^2\right) , \qquad (10)$$

where R is the distance between the RE and the ligand (e.g. R = 2.52 Å in Sm₂Fe₁₇N₃). 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 Å⁻¹. This result is in agreement with q = 2 Å⁻¹ for iron and q = 2.5 Å⁻¹ for iron-rich RE intermetallics. The model was not applied to the carbides because in that case a stronger hybridization is expected.

For $Dy_2Fe_{17}N_3$ ($\mathcal{J} = \frac{15}{2}$) 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{I} -mixing and nonlinear effects have been neglected.

References

- J. M. D. Coey and H. Sun, J. Magn. Magn. Mat., vol. 87, pp. L251–L254, 1990.
- [2] G. Asti, R. Cabassi, F. Bolzoni, S. Wirth, D. Eckert, P. A. P. Wendhausen and K.-H. Müller, J. Appl. Phys., vol. 76, pp. 6268–6270, 1994.
- [3] H.-S. Li and J. M. Cadogan, Solid State Comm., vol. 80, no. 11, pp. 905-908, 1991.
- [4] H. Kato, M. Yamada, G. Kido and Y. Nakagawa, J. Appl. Phys., vol. 73, pp. 6931-6933, 1993.
- [5] M. D. Kuz'min and J. M. D. Coey, Phys. Rev. B, vol. 50, pp. 12533-12539, 1994.
- [6] H.-S. Li and J. M. Cadogan, Solid State Comm., vol. 82, no. 2, pp. 121-125, 1992.
- [7] T. S. Zhao, X. C. Kou, R. Grössinger and H. R. Kirchmayr, *Phys. Rev. B*, vol. 44, pp. 2846–2849, 1991.
- [8] M. T. Hutchings, in *Solid State Physics*, vol. 16, F. Seitz and D. Turnbull, Eds. New York: Academic, 1964, pp. 227-273.
- [9] A. J. Freeman and R. E. Watson, Phys. Rev., vol. 127, pp. 2058-2075, 1962.
- [10] M. D. Kuz'min, Phys. Rev. B, vol. 46, pp. 8219-8226, 1992.
- [11] R. Skomski, in Interstitial Intermetallic Alloys, Eds. F. Grandjean, G. J. Long, and K. H. J. Buschow, Kluwer, Dortrecht 1995, pp.561-598.
- [12] R. Skomski, Phil. Mag. B, vol. 70, no. 2, pp. 175-189, 1994.