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Crystal field in nitrogenated rare-earth intermetallics

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The crystal-field in $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ and $\text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{1-\delta}$ due to interstitial nitrogen has been investigated. Intrinsic parametrization in the superposition model allows separation of the crystal field created by a neighboring nitrogen atom from a purely geometrical factor, which is different for $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ and $\text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{1-\delta}$. Using published magnetic data, values for the intrinsic parameter A_2 per nitrogen atom of $A_2 = 200 \pm 60 \text{ K}a_0^{-2}$ and $A_2 = 270 \pm 60 \text{ K}a_0^{-2}$ for $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ and $\text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{1-\delta}$, respectively, are obtained. Because of charge penetration, which is discussed in the form of an explicit crystal-field weight function, it is not possible to interpret A_2^0 or A_2 as crystal-field parameters independent of the $4f$ ion.

I. INTRODUCTION

The discovery that nitrogen or carbon absorption drastically improves the magnetic properties of $\text{Sm}_2\text{Fe}_{17}$ has sparked interest in the gas-phase interstitial modification of rare-earth intermetallics. Interstitial modification leads to a volume expansion of about 6%, which is the main cause for the improvement of saturation magnetization and Curie temperature of $\text{Sm}_2\text{Fe}_{17}$ (see Refs. 1 and 2). However, the change from easy-plane to strong easy-axis anisotropy is ascribed to the modification of the rare-earth crystal field due to the surrounding nitrogen or carbon atoms.^{1,2} Another example of interstitial modification of a rare-earth intermetallic is easy axis $\text{Sm}(\text{Fe}_{11}\text{Ti})$, whose nitride $\text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{1-\delta}$ shows easy-plane anisotropy.³

Interstitial nitrogen atoms in $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ and $\text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{1-\delta}$ occupy the large octahedral $9e$ sites in the $\text{Th}_2\text{Zn}_{17}$ structure and $2b$ sites in the ThMn_{12} structure nearly exclusively.^{2,3} The coordination of rare-earth atoms by neighboring interstitials is different in the two structures; the $9e$ sites form an in-plane triangle, whereas the $2b$ sites form an axial dumbbell (Fig. 1). This provides a qualitative explanation of the observed anisotropy trends, if we take into account the electrostatic repulsion between the prolate Sm^{3+} $4f$ shell and negatively charged interstitial atoms.

Here, we use the intrinsic parametrization of the superposition model⁴ to separate the effect of the geometric arrangement of the nitrogen atoms (Fig. 1) from the underlying strength of the crystal field created by a single nitrogen atom.

II. MODEL AND CALCULATION

The following assumptions are made.

(i) The compound consists of two sublattices: a ferromagnetic Fe sublattice with the magnetization \mathbf{M}_{Fe} and a paramagnetic Sm sublattice exposed to the Sm-Fe exchange field $\mathbf{B}_{\text{ex}} = n_{\text{Sm-Fe}}\mu_0\mathbf{M}_{\text{Fe}}$. The Sm-Sm exchange is neglected, while the Sm-Fe exchange is assumed to be isotropic. The Sm anisotropy is believed to originate from the electrostatic crystal field acting on the $4f$ shells of the Sm^{3+} ions in their $J=5/2$ ground state; J -mixing effects are neglected. The crystal-field interaction is treated as a perturbation with respect to the Sm-Fe exchange, so the

unperturbed $4f$ wave functions can be used to calculate the crystal-field energy.

(ii) At room temperature, only the lowest-order crystal-field interaction parameter A_2^0 is taken into account.⁵ To describe the rare-earth crystal-field interaction we use the notation⁶

$$\mathbb{H}_{\text{CF}} = \alpha_f A_2^0 \langle r^2 \rangle O_2^0 \quad (1)$$

The temperature dependence of the Stevens operator expressions has been treated by Kuz'min who finds

$$\langle O_2^0 \rangle = \frac{25}{2} B_{5/2}^2 \left(\frac{25 n_{\text{R-Fe}} \mu_0 \mathbf{M}_{\text{Fe}}}{7 kT} \right) \quad (2)$$

and

$$K_1 = K_{\text{Fe}} - \frac{65}{84} A_2^0 \langle r^2 \rangle B_{5/2}^2 \left(\frac{25 n_{\text{R-Fe}} \mu_0 \mathbf{M}_{\text{Fe}}}{7 kT} \right), \quad (3)$$

where $B_{5/2}^2(x)$ is the second-order generalized Brillouin function.⁷ As can be seen from Fig. 2, the generalized Brillouin function yields a low-temperature plateau (solid line), whereas the classical Bessel function (dashed lines) fails to match the two observed data points.^{8,9}

(iii) The crystal field is supposed to be the sum of independent contributions from all the nearest nitrogen neighbors.⁴ To separate explicitly the purely geometrical effect, we introduce the intrinsic parameter A_2 , which describes the crystal-field change per nitrogen atom

$$A_2^0(c) = A_2^0(0) + \frac{1}{2} c \zeta (3 \cos^2 \theta - 1) \tilde{A}_2. \quad (4)$$

Here, c is the nitrogen concentration on the interstitial sites, ζ the number of interstitial next neighbors, and θ the

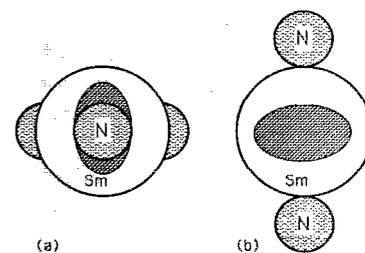


FIG. 1. The coordination of interstitial nitrogen in (a) $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ ($\theta = \pi/2$) and (b) $\text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{1-\delta}$ ($\theta = 0$).

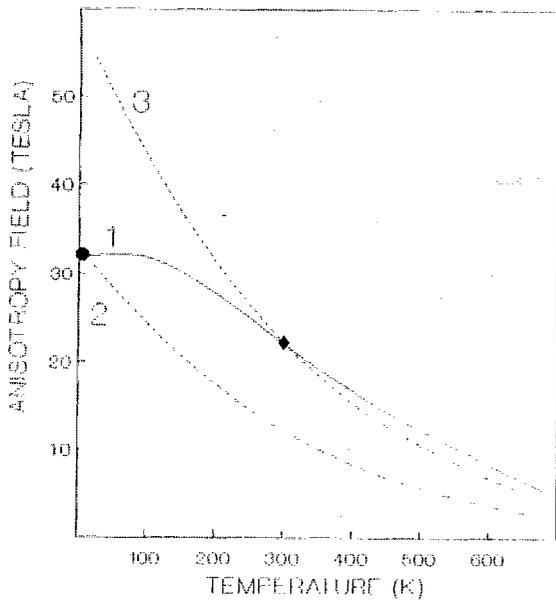


FIG. 2. Temperature dependence of the anisotropy field of $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$. Solid line (curve 1): calculated using Eq. (2) with $A_2^0 = -340 \text{ K}a_0^{-2}$. Dashed lines: calculated using the classical Bessel function $\hat{I}_{5/2}(x)$ instead of $B_{5/2}^2(x)$ in Eq. (2) with $A_2^0 = -280 \text{ K}a_0^{-2}$ (curve 2) and $A_2^0 = -480 \text{ K}a_0^{-2}$ (curve 3). Experimental data: Ref. 7 (circle) and Ref. 8 (square).

corresponding coordination angle, $\theta[\text{Sm}(\text{Fe}_{11}\text{Ti})] = 0$ and $\theta(\text{Sm}_2\text{Fe}_{17}) = \pi/2$ (Fig. 1). To deduce A_2 from Eq. (4), we have to compare $A_2^0(c)$ for at least two different nitrogen concentrations, c and 0. With the anisotropy field $H_a = 2K_1/\mu_0 M_0$, we obtain

$$\tilde{A}_2 = -\frac{2\mu_0[(M_0 H_a / v_R)_c - (M_0 H_a / v_R)_0]}{3\alpha_f(3 \cos^2 \theta - 1)c \langle r^2 \rangle \langle O_2^0(c) \rangle}, \quad (5)$$

where v_R denotes the density N_R/V of rare-earth atoms.

To determine $\langle O_2^0 \rangle$ the molecular field constants $n_{\text{R-Fe}}$ must be known: $n_{\text{R-Fe}}(\text{R}_2\text{Fe}_{17}) = 300 \mu_0$ and $n_{\text{R-Fe}}(\text{RFe}_{11}\text{Ti}) = 340 \mu_0$ (see Refs. 10 and 11). We will make use of the value $A_2^0(3c = 2.80 \pm 0.15) = -242 \text{ K}/a_0^2$ deduced from the room-temperature anisotropy field $\mu_0 H_a = 22 \text{ T}$. Similar considerations yield $A_2^0(c=0) = 35 \text{ K}/a_0^2$ for the parent compound $\text{Sm}_2\text{Fe}_{17}$ ($\mu_0 H_a = -4 \text{ T}$) (see Ref. 9). The values used for $\text{Sm}(\text{Fe}_{11}\text{Ti})$ are $A_2^0(c=0) = -135 \text{ K}/a_0^2$ and $A_2^0(c=0.8) = 292 \text{ K}/a_0^2$ (cf. Ref. 3 and 9). Finally, we obtain for the intrinsic crystal-field per nitrogen atom

$$\tilde{A}_2 = +200 \pm 60 \text{ K}a_0^{-2}, \quad \text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}, \quad (6a)$$

$$\tilde{A}_2 = +270 \pm 60 \text{ K}a_0^{-2}, \quad \text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{1-\delta}, \quad (6b)$$

where the estimated error includes the uncertainty in c , H_a and $\langle O_2^0 \rangle$.

III. DISCUSSION

A. Sign and magnitude of \tilde{A}_2

The intrinsic parameters Eq. (6) have the same sign and similar numerical values, although the corresponding anisotropy field values are completely different. This con-

firms the idea that the crystal-field modification in $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ and $\text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{1-\delta}$ is directly due to neighboring nitrogen atoms. Note that electrostatic charges are strongly screened in metals, as opposed to non-metallic rare-earth compounds, where the lattice summation is much more difficult (cf. Ref. 4).

It is interesting to compare the present results with data available from literature. Equation (4) predicts a linear increase of A_2^0 with the interstitial concentration c . Mössbauer and magnetic measurements on $\text{Sm}_2\text{Fe}_{17}$ carbides and nitrides indicate a concentration dependence which is, at least approximately, linear,^{9,12,13} but the quantitative situation is less satisfactory. From Ref. 12, an intrinsic crystal field of $A_2 = +126 \text{ K}a_0^{-2}$ can be deduced for $\text{Sm}_2\text{Fe}_{17}$ nitride and carbide, but extrapolation of the experimental data yields $A_2^0(\text{Sm}_2\text{Fe}_{17}\text{N}_{y \rightarrow 0}) \approx -50 \text{ K}a_0^{-2}$ and $A_2^0(\text{Sm}_2\text{Fe}_{17}\text{C}_{y \rightarrow 0}) \approx 0$. A possible reason for this inconsistency are inexact concentration values c .

It is difficult to decide whether the difference between the two values (6a) and (6b) is significant. Taking into account the distance dependence of the crystal field ($A_2 \propto 1/R^3$ in the point-charge model) and the slightly smaller samarium-nitrogen distance in the 1-12 lattice (5%), we should expect a difference of about $30 \text{ K}a_0^{-2}$.

B. Crystal-field interaction

The electrostatic crystal-field energy, which includes charge penetration, is given by

$$H_{\text{CF}} = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r})\rho_{4f}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (7)$$

where $\rho_{4f}(\mathbf{r})$ and $\rho(\mathbf{r})$ are the local $4f$ density and the density of the non- $4f$ electrons, respectively. Like any other functions, $\rho_{4f}(\mathbf{r})$ and $1/|\mathbf{r}-\mathbf{r}'|$ can be expanded in spherical harmonics. The result is a sum of six-fold integrals, each of them yielding a crystal-field parameter. If $\rho(\mathbf{r})$ is known, e.g., from band structure calculations, these integrals can be solved numerically. To obtain a more physical interpretation of the crystal-field integrals, we represent A_2^0 as a three-fold integral

$$A_2^0 = - \int (3 \cos^2 \theta - 1) W_2(r) \rho(r) dr, \quad (8)$$

where the crystal-field weight function

$$W_2(r) = \frac{e}{4\pi\epsilon_0} \frac{1}{4\langle r^2 \rangle} \left(\int_0^r \frac{\xi^4}{r^3} F(\xi) d\xi + \int_r^\infty \frac{r^2}{\xi} F(\xi) d\xi \right) \quad (9)$$

is characteristic of a given rare-earth metal. Therefore A_2^0 explicitly depends on the $4f$ charge distribution. Figure 3 shows the function $W_2(r)$ for samarium, derived from Hartree-Fock $4f$ charge density values.¹⁴ If the source of the crystal field is far away from the rare-earth ion, the $1/r^3$ dependence of the point-charge model is reproduced. For distances below 0.5 \AA the crystal-field interaction is much less than expected from the point-charge model.

In the case of point-charge like non- $4f$ charge clouds the radial dependence of the crystal field is given by Fig. 3

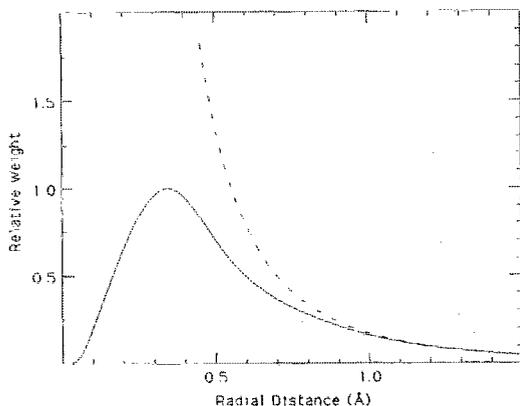


FIG. 3. Radial weight function $W_2(r)$ for the second-order crystal-field interaction.

(solid line). Assuming an effective point charge $q_0 = -3e$ per nitrogen atom and a Sm-N distance of about 2.45 \AA , we obtain $A_2 = 4500 \text{ Ka}_0^{-2}$. In reality, this large value is reduced by screening and polarization effects to about 5% of this value.

In Ref. 12, the crystal-field modification is ascribed to fractional bonds¹⁵ and fictitious charge transfer from nitrogen to samarium. With a nitrogen single-bond distance of $d_N(1) = 0.55 \text{ \AA}$, the authors were able to achieve excellent agreement between measured and calculated A_2^0 values for $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$, but the more realistic value $d_N(1) = 0.74 \text{ \AA}$ ¹⁵ yields a factor 2.1.

Coehoorn *et al.* investigated the crystal-field contribution of the $5d$ and $6p$ electrons and found considerable deviations from the point-charge model behavior.^{16,17} Figure 3 gives an illustrative interpretation of this behavior: due to the strong overlap between valence and $4f$ electrons,¹⁴ a part of the valence electrons can be found at $r < 0.5 \text{ \AA}$ where the point-charge model fails. The observed anisotropy trends are explained by the continuity of the electron density at the Wigner-Seitz cell boundary, as opposed to Ref. 12, where the electronegativity difference is the main factor.

IV. CONCLUSIONS

The intrinsic crystal field contribution per nitrogen atom (ca. 200 Ka_0^{-2}) is comparable in $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ and $\text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{1-\delta}$, which indicates that the nitrogen provides a common mechanism of crystal-field modification in both compounds. A crystal-field weight function is introduced to show that charge penetration is negligible for a localized interstitial, but is important as far as polarization of non- $4f$ orbitals is concerned.

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