

Temperature Dependence of the Crystal-Field-Induced Anisotropy in SmFe_2

A. M. van Diepen

Philips Research Laboratories, Eindhoven, The Netherlands

H. W. de Wijn

Fysisch Laboratorium der Rijksuniversiteit, Utrecht, The Netherlands

K. H. J. Buschow

Philips Research Laboratories, Eindhoven, The Netherlands

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For the compound SmFe_2 , ^{57}Fe Mössbauer spectra were obtained at various temperatures between 5 and 300 K. We observed that the axis of easy magnetization changes from [011] below about 175 K to [111] above this temperature. We have calculated the single-ion crystal-field magnetic anisotropy of Sm^{3+} , with the inclusion of effects of exchange, and have found this model to account well for the transition in the direction of easy magnetization.

I. INTRODUCTION

The cubic Laves-phase compounds of iron and rare-earth elements $R\text{Fe}_2$ (R = rare earth) have magnetic ordering temperatures ranging from 545 K (YFe_2) to 785 K (GdFe_2). The dominant exchange interaction in these compounds is between the iron moments and it is ferromagnetic. The weaker antiferromagnetic coupling between the iron moment and the rare-earth spin moment leads to a ferrimagnetic arrangement at low temperatures.^{1,2} Bowden *et al.*³ investigated the Mössbauer spectra of these compounds. With the exception of SmFe_2 and GdFe_2 , which showed a complex behavior, they found the direction of the magnetization to be, dependent on R , along [001] or [111]. This could be accounted for in terms of crystalline single-ion anisotropy on the R site. Recently, this investigation has been extended by Atzmony *et al.*⁴ to pseudobinary compounds of the type $\text{Ho}_x\text{Tb}_{1-x}\text{Fe}_2$, in which they studied the variation of the easy direction as a function of the concentration x as well as the temperature T . In particular, for the range of medium concentration, they observed a change in easy direction from [011] at low temperatures to [111] at high temperatures. This transition was discussed by them in terms of the free energy calculated as a function of x and T .

In the present investigation we report on the temperature dependence of the direction of easy magnetization for the compound SmFe_2 . As distinct from the other $R\text{Fe}_2$, the magnetization of SmFe_2 stabilizes at low temperatures along [011]. Above about 175 K the easy direction has moved over to [111]. Although SmFe_2 is a purely binary compound, its behavior is similar to the above-mentioned pseudobinary compounds with intermediate x . In the spirit of Bowden *et al.* we have attributed the occurrence of different directions of magnetization to single-ion crystal-field anisotropy at the Sm site.

The calculation, however, cannot be based on the ground J state only, as in the previous cases, since both crystal and exchange fields will mix the closeby $J = \frac{7}{2}$ and higher states into the ground $J = \frac{5}{2}$ state of Sm^{3+} . Taking this admixture into account, we have calculated the free energy of Sm^{3+} as a function of the temperature with the molecular field in various crystallographic directions. The results of these calculations will be compared with the experimental data.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The compound SmFe_2 was prepared by sealing Sm metal (99.9% pure) and Fe powder (99.99% pure) into a Mo container, subsequent heating for 10 min at a temperature above the melting point of Sm, and vacuum annealing for three weeks at 850°C. The x-ray-diffraction powder diagram taken after annealing showed that the sample was single-phase cubic MgCu_2 structure.

The ^{57}Fe Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer. The source, consisting of ^{57}Co in Pd and kept at room temperature, was moved, while the absorber remained at a fixed position. The absorber consisted of 40-mg/cm² SmFe_2 powder glued to Fe-free mica by means of an acetone-based glue. The spectrometer was calibrated with reference to ^{57}Fe spectra in iron foil. The spectra taken at 5 and 78 K were obtained by use of a cold-finger cryostat. For the spectra taken between room temperature and 78 K, temperatures were stabilized by regulating a flow of boiled-off nitrogen gas by means of a feedback system. A carbon resistor and a silver-constantan thermocouple were used to measure the temperature. Two types of spectra were observed, each type consisting of two six-line patterns. Some characteristics of these spectra

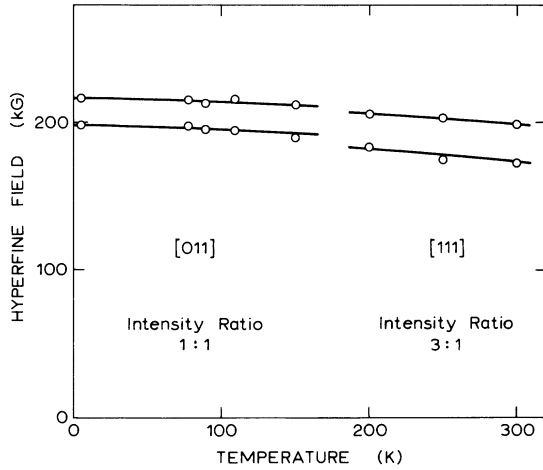


FIG. 1. Hyperfine fields at ^{57}Fe nuclei in SmFe_2 as a function of temperature. Below 150 K spectra consisting of two six-line patterns of equal intensity are observed, indicating [011] as preferred direction. Above 200 K two six-line patterns with intensity ratio 3 (upper curve) to 1 (lower curve) are observed, showing that the easy axis has moved to [111]. The transition from [011] to [111], occurring around 175 K, is of gradual nature.

are gathered in Fig. 1.

Below 150 K the two six-line patterns were well defined and of equal intensity. Upon increasing the temperature above 150 K, the spectra modified, until at 200 K they again were well defined but with a 3:1 intensity ratio of the two six-line patterns. In Fig. 1 we show the hyperfine fields corresponding to each six-line pattern as determined from the outermost peaks. In SmFe_2 the Sm atoms reside on a diamond-type lattice, whereas the Fe atoms occupy corner-sharing tetrahedral networks. The point symmetry of each iron atom is $\bar{3}m$ with the threefold axis along the [111] direction. For a moment direction other than [001] the presence of a nonzero quadrupole coupling results in inequivalence of the iron sites, because the angles between the direction of the local magnetic field and the symmetry axis of the electric field gradient, [111], differ. The observed spectra are consistent with a [011] axis of easy magnetization below 150 K, and [111] above 200 K. The transition, occurring around 175 K, seems to be of a gradual nature. Bowden *et al.*³ have tentatively concluded from their Mössbauer data that at 77 K the direction of magnetization would be along [011]. This agrees with the present results.

III. CALCULATIONS

In this section we calculate the magnetic anisotropy of Sm^{3+} ions ($4f^5$; $L=5$, $S=\frac{5}{2}$) subject to cubic crystalline fields and a molecular field. First

we calculate the energy levels of the Sm^{3+} ion starting with the Hamiltonian

$$\mathcal{H} = \lambda \vec{L} \cdot \vec{S} + \mathcal{H}_c + 2\mu_B \vec{H}_{\text{ex}} \cdot \vec{S} \quad (1)$$

The first term represents the spin-orbit coupling, where we have used $\lambda/k_B = 410$ K throughout the calculations. The molecular field H_{ex} , exerted on the Sm^{3+} by other Sm ions and the Fe ions, is chosen to point parallel to the [001], [011], or [111] direction. For the single-ion crystalline-field energy we have

$$\mathcal{H}_c = A_4 \sum_i (f_{40} + 5f_{44}) + A_6 \sum_i (f_{60} - 21f_{64}), \quad (2)$$

where the z axis is taken parallel to one of the cube axes [001], and the summations are carried over all 4f electrons. The functions f_{kq} , defined through

$$c_{k0} f_{k0}(\vec{r}) = r^k Y_k^0(\theta, \varphi), \quad (3a)$$

$$c_{kq} f_{kq}(\vec{r}) = 2^{-1/2} r^k [Y_k^{-q}(\theta, \varphi) + (-1)^q Y_k^q(\theta, \varphi)] \quad (q > 0) \quad (3b)$$

and their normalization constants c_{kq} , have been listed by Hutchings.⁵ For the case of Sm^{3+} , the evaluation of the matrix elements of Y_k^q between any J and J' has been described by us in a previous paper.⁶ All matrix elements, both diagonal and off diagonal, within and between the ground state $J = \frac{7}{2}$ and the first two excited states $J = \frac{7}{2}$ and $\frac{5}{2}$, have been included in the diagonalization of Eq. (1). In case H_{ex} is parallel to [011] or [111], we have first transformed the z axis from [001] to parallel to H_{ex} before diagonalization.

Using various values for the crystal-field parameters $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$, and the exchange field H_{ex} , we have computed the energy levels of a Sm^{3+} ion for the three possible directions of magnetization. Subsequently, we have calculated the partition function Z , and the Helmholtz free energy $F = -k_B T \ln Z$. For a given set of the parameters $A_4 \langle r^4 \rangle$, $A_6 \langle r^6 \rangle$, and H_{ex} , and a given temperature T , the easy axis of magnetization is then determined as the direction for which F reaches the lowest value.

The direction of the easy axis of magnetization as a function of the crystal-field parameters at various temperatures is shown in Figs. 2 and 3 for $\mu_B H_{\text{ex}}/k_B = 65$ and 130 K, respectively. It is observed that the combined fourth- and sixth-order crystal fields result in three regions. In the origin of the easy-axis diagrams, where the Sm^{3+} magnetocrystalline anisotropy disappears, these regions, of course, merge. Upon comparing the diagrams we further note that the shape and extent of the [011] region are particularly sensitive to temperature and exchange field. In Fig. 4 the dependence of the transition temperature from [011] to [111] on the exchange field is shown for $A_4 \langle r^4 \rangle/k_B = +100$ K and $A_6 \langle r^6 \rangle/k_B = -100$ K as an example.

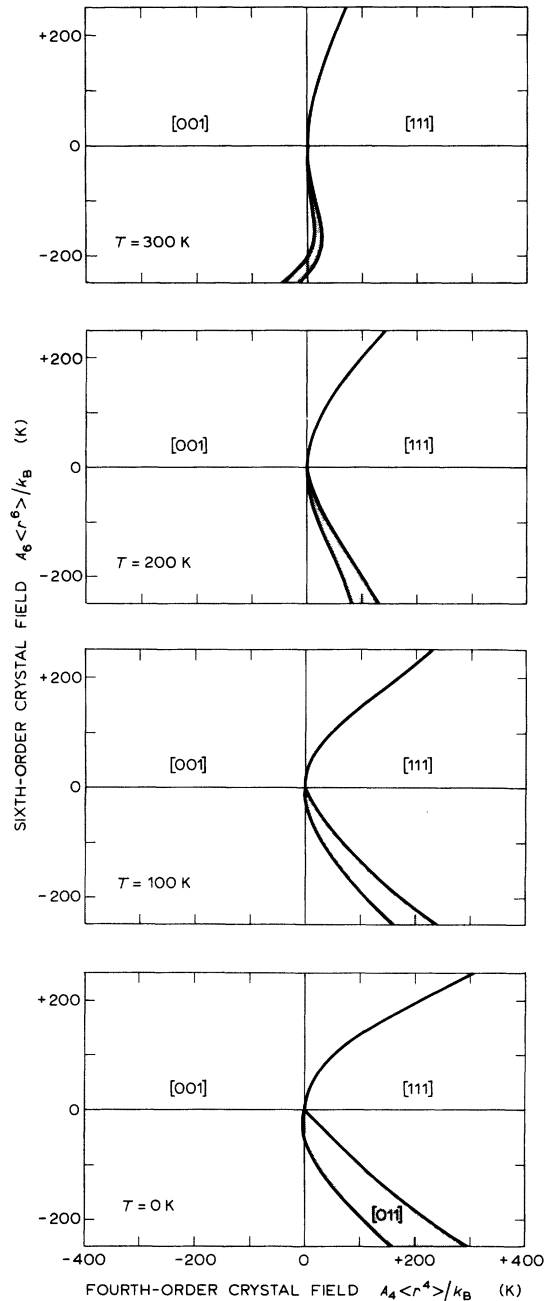


FIG. 2. Easy-axis diagram. Direction of the easy axis as a function of the crystal-field parameters $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ for a constant exchange field $\mu_B H_{\text{ex}} / k_B = 65$ K at various temperatures.

IV. DISCUSSION

By use of the results shown in Figs. 2 and 3 it is possible, in principle, to predict the direction of easy magnetization for a given set of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$. Also, the results can serve to find out whether temperature variation leads to a change in

the easy direction. The quantities $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ depend on details of the crystal structure, and we will treat them as parameters.

An estimate for the parameter H_{ex} can be obtained from the observed magnetic ordering temperature of the compound. In SmFe_2 the situation is somewhat complex, however, because the ex-

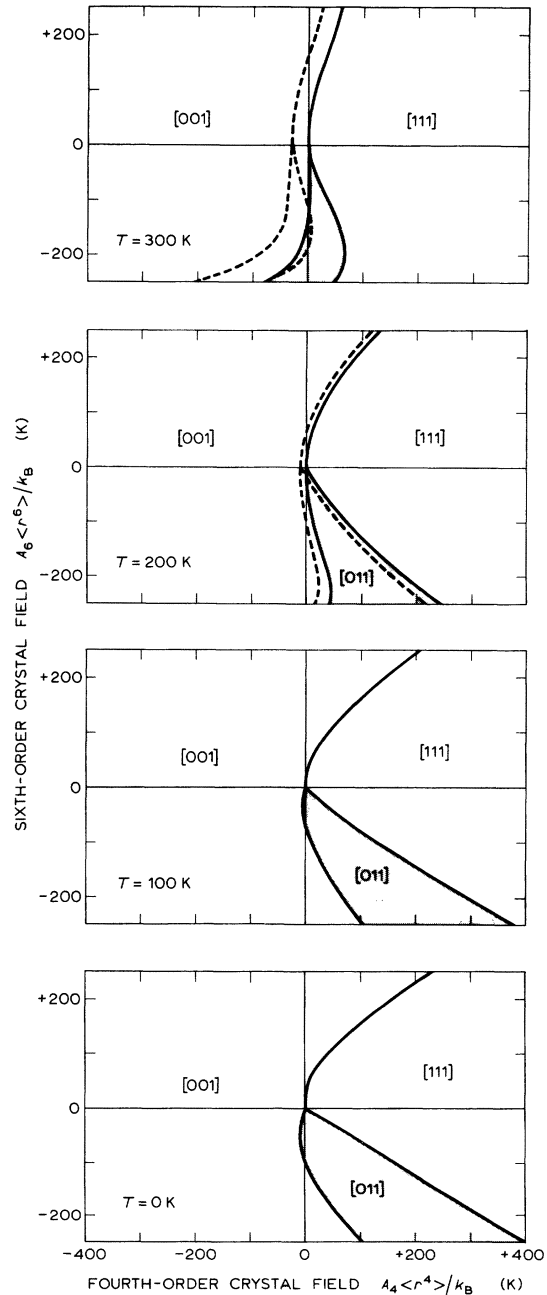


FIG. 3. Easy-axis diagram for $\mu_B H_{\text{ex}} / k_B = 130$ K at various temperatures. The dashed lines indicate the transitions with an additional bulk anisotropy of $K_1 / k_B = -2$ K per formula unit.

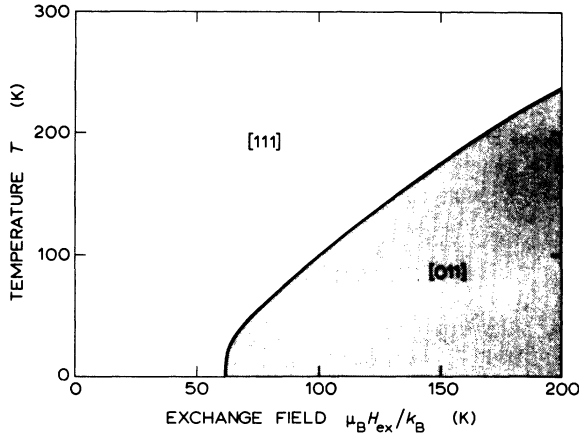


FIG. 4. Effect of exchange on the transition temperature, where the direction of easy magnetization changes from [011] to [111], for crystal-field parameters $A_4 \langle r^4 \rangle / k_B = +100$ K and $A_6 \langle r^6 \rangle / k_B = -100$ K, as an example.

change field experienced by the Sm ions originate not only from the Sm-Fe interaction, but also from the weaker Sm-Sm interaction. In the molecular field approximation the Curie temperature T_C is⁷

$$T_C = \frac{1}{2} \{ C_1 W_{11} + C_2 W_{22} + [(C_1 W_{11} - C_2 W_{22})^2 + 4C_1 C_2 W_{12}^2]^{1/2} \}, \quad (4)$$

where C_1 and C_2 are the Curie constants of the Fe and Sm sublattices. The quantities W_{11} , W_{22} , and W_{12} are the molecular field parameters referring to the exchange interaction within the Fe sublattice, within the Sm sublattice, and between the Sm and Fe sublattices, respectively. Of these, the interaction within the Fe sublattice is the dominant one. The exchange field acting on the Sm ions is estimated as follows. In the RNi_2 compounds, isostructural with $SmFe_2$, the Ni atoms do not carry a magnetic moment, so that we have $C_1 = 0$ and $T_C = C_2 W_{22} = W_{22} G \mu_B / k_B$ with $G = \frac{1}{3} (g-1)^2 J(J+1)$. By plotting the T_C values of the series RNi_2 versus the G values of the corresponding R , we find $W_{22} \mu_B^2 / k_B = 15$ K. For YFe_2 we have $C_2 = 0$ and $T_C = C_1 W_{11} = 545$ K.¹ From Eq. (4) it follows that in the RFe_2 compounds the contribution to T_C from the R - R interaction is approximately $(C_2 W_{22})^2 / 4C_1 W_{11}$, which amounts to only 3 K in the case of $GdFe_2$ and is negligible for the other RFe_2 . Further analysis of the T_C 's of the known RFe_2 compounds as a function of G of the corresponding R results

in a molecular field of magnitude $|\mu_B H_{ex} / k_B| \approx 130$ K. From the magnetization of $SmFe_2$ ($T_C = 676$ K), as well as the hyperfine fields (Fig. 1), it is inferred that this value is virtually independent of temperature below, say, 200 K.

The results shown in Fig. 3 therefore seem appropriate for application to $SmFe_2$. The requirement set by experiment, a change of the easy direction from [011] to [111] near 175 K, is satisfied for $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ values of roughly the same magnitude, with the former positive and the latter negative. Examination of Figs. 2 and 4 shows that this conclusion is not very sensitive to the choice made for H_{ex} . Here, no account has been taken of the Fe sublattice anisotropy. This anisotropy may be studied in YFe_2 , where according to the results of Bowden *et al.*³ the easy direction points along [111]. At 4.2 K the magnetization becomes saturated in magnetic fields over a few kG, which can be regarded as a measure of the upper limit for the anisotropy energy. The correction of the free energy favoring [111] relative to [011] in $SmFe_2$ can therefore be estimated to be of the order of 0.1 K per formula unit. In terms of Figs. 2 and 3 this implies a growth of the area designated by [111]. In Fig. 3, the dashed lines indicate the calculated effect of a bulk anisotropy with $K_1 / k_B = -2$ K per formula unit ($K_1 \approx -6 \times 10^6$ erg/cm³), corresponding to a difference in free energy between [011] and [111] of 0.17 K per formula unit. At $T = 100$ K and below the anisotropy due to the Fe sublattice is completely negligible with respect to the Sm^{3+} single-ion anisotropy.

V. CONCLUSION

It has been shown that with reasonable assumptions regarding the exchange field acting on the Sm ions it is possible to designate a distribution of sets of crystal-field parameters which is in keeping with the observed change in easy direction near 175 K: $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ are apparently of roughly the same magnitude, while the former is positive and the latter negative. The importance of sixth-order terms emerges clearly from the present results: A fourth-order crystal field would favor either the [111] or the [001] direction (see Figs. 2 and 3), whereas a [011] easy direction entails a nonzero value of the sixth-order term. Since the sixth-order field has zero matrix elements within the $J = \frac{5}{2}$ ground state, this, in turn, also shows the importance of including the $J = \frac{7}{2}$ and higher excited states.

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Electric Field Effect on the Elastic Constant near the Gadolinium Molybdate Phase Transition

J. M. Courdille and J. Dumas

Laboratoire d'Ultrasons,* Université Paris VI,
Tour 13, 11, quai Saint-Bernard, 75230 Paris-Cedex 05, France
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The elastic constant c_{11} of gadolinium molybdate varies with the electric field [$c_{11}(E) = c_{11}(E=0) + \beta_{311}E$]. In the vicinity of the 159°C ferroelastic phase transition, the critical exponent n , in the variation of coefficient β_{311} with temperature, was found to be 1.0 ± 0.2 . A shift in the transition temperature, under the action of an electric field, is observed indirectly.

Above 159°C gadolinium molybdate (GMO) belongs to the $42m$ class of tetragonal system and is a paraelectric crystal.¹ Below this temperature, it becomes ferroelectric-ferroelastic and it belongs to the $mm2$ symmetry class of orthorhombic system.² The first-order type of transition is now well established.³ The critical behavior of the second-order derivative of the free energy, involving the electric field and the strain, has already been studied.⁴⁻⁶ The values of several elastic constants show a jump near T_c ,⁶ but the dielectric constant remains unchanged in the high-temperature phase: This is characteristic of an improper ferroelectric crystal.⁷ Recently,⁵ the piezoelectric constant \tilde{d}_{38} ⁸ has been measured near T_c , revealing an anomalous increase.

In this paper, experiments are presented showing the variations with temperature of the third-order coefficient β_{311} , giving the variation of the elastic constant c_{11} with the electric field E_3 . In the thermodynamic potential, it corresponds to the term $\beta_{311}u_1^2 E_3$, where u_1 is the longitudinal strain along the a orthorhombic axis and E_3 is the static electric field along c axis. β is thus a fifth-rank tensor.

The elastic constant which is given by the second-order derivative of the potential relative to the strain, becomes, in the presence of an electric field, $c_{11} + 2\beta_{311}E_3$.

Measurements have been made using pulse-echo technique. A 560-MHZ ultrasonic longitudinal wave was propagated along the GMO a axis. The phase of this wave after crossing the crystal was compared with that of a reference wave. The relative sensitivity of the method was 10^{-4} . The whole temperature device was controlled and regulated

to limit fluctuations to less than 0.05°C. The ultrasonic phase shift was displayed as a function of the electric field applied along the c axis of the crystal. The coefficient β for a given temperature is related to the phase shift. All measurements are given for a same field value, 8.75 kV/cm.

In this two-wave interferometric method, the phase shift is given by

$$\Delta\psi = \omega\Delta \frac{l}{v} = \frac{l\omega}{v} \frac{\Delta l}{l} - \frac{\Delta v}{v},$$

where ω is the ultrasonic frequency, l is the crystal length, v is the ultrasonic velocity, and Δl and Δv are crystal-length and sound-velocity variations under the applied field. Thus the change of phase of the acoustic wave is composed of two factors: one resulting from a dilatation of the crystal and depending on the d_{31} piezoelectric and g_{331} electrostrictive coefficients, and the other being due to the change of the elastic constants with the electric field. In terms of these different coefficients, one may write

$$\Delta\psi = (l\omega/v) [d_{31} + g_{331} E_3 - \beta_{311}/c_{11}] E_3.$$

Dilatation experiments on the same crystals have shown that the influence of $\Delta l/l$ on $\Delta\psi$ is negligible compared with that of the second term $\Delta v/v = -(\beta_{311}/c_{11})E_3$. Recently published measurements on piezoelectric⁵ and electrostrictive coefficients³ in GMO have confirmed our conclusions.

Figure 1 shows the coefficient β_{311} plotted as a function of temperature. It reveals a large anomaly in the vicinity of the phase transition. In this experiment the transition temperature is difficult to observe since over a range of 3 or 4°C it was not possible to follow the signal, owing to the very important ultrasonic attenuation.