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Exchange and crystal field in Sm-based magnets. I. Inelastic neutron scattering and high-field magnetization study of Sm_2Fe_{17} and $Sm_2Fe_{17}N_3$

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A peak is detected in the high-energy inelastic neutron scattering spectra of Sm_2Fe_{17} and $Sm_2Fe_{17}N_3$, which is associated with the intermultiplet transition in the $4f$ shell of samarium. The peak in the nitride $Sm_2Fe_{17}N_3$ is situated at a lower energy (163 meV) as compared with the parent compound Sm_2Fe_{17} (177 meV). The peak position provides direct information on the strength of the exchange field on Sm in both compounds: $B_{ex} = 380$ and 270 T in Sm_2Fe_{17} and $Sm_2Fe_{17}N_3$, respectively. The 30% reduction in B_{ex} as a result of nitrogenating Sm_2Fe_{17} is consistent with the earlier discovered similar effect in Gd_2Fe_{17}. High-field ($B \leqslant 50$ T) magnetization curves have been measured on an oriented powder sample of $Sm_2Fe_{17}N_3$ and analyzed using the newly determined B_{ex}. The leading crystal field parameter is thus found to be $A_2^0\langle r^2\rangle = -28$ meV.

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I. INTRODUCTION

Nitrogenation of Sm_2Fe_{17} dramatically modifies its properties, making it one of the most promising candidates for permanent magnet materials. The improvement is twofold: a higher Curie point and a large negative leading crystal field parameter A_2^0.[1] Relatively little is known about the effect of nitrogenation on the exchange field B_{ex} acting on the $4f$ shell of Sm, despite the fact that at temperatures relevant to industrial applications this parameter is an important ingredient of the magnetic anisotropy (roughly speaking, above room temperature, $K_1 \propto A_2^0 B_{ex}^2$). Inelastic neutron scattering (INS) experiments on the isostructural Gd system revealed a 30% drop in the low-temperature value of the exchange field, $B_{ex}(0)$, upon nitrogenation;[2] i.e., the quantity $B_{ex}^2(0)$ was halved. At elevated temperatures B_{ex} scales down approximately as the iron sublattice magnetization, $B_{ex}(T) \approx B_{ex}(0)\ \sigma_{Fe}(T/T_C)$, where $\sigma_{Fe}(x)$ is a universal dimensionless function, $\sigma_{Fe}(0) = 1$. Thus the drop in $B_{ex}^2(0)$ may or may not be outweighed by the rise in T_C. To obtain direct quantitative information on the size of the effect in the $Sm_2Fe_{17}N_x$ system is therefore of topical interest.

With this end in view we set out to perform INS experiments on $Sm_2Fe_{17}N_3$ as well as on the parent system Sm_2Fe_{17}. These were complemented by high-field magnetization measurements on oriented $Sm_2Fe_{17}N_3$ powder samples. The experimental procedures are described in the following section. Two subsequent sections are dedicated to the analysis of the INS and magnetization data, resulting in estimates of B_{ex} and A_2^0, respectively. The final section contains a discussion of the obtained results.

II. EXPERIMENTAL DETAILS

Sm_2Fe_{17} was produced by arc melting in Ar atmosphere, under a pressure of 0.7 bar. The initial components were 99.9%-pure iron and 98.9%-pure samarium isotop ^{154}Sm, the latter material containing no more than 0.06% of ^{149}Sm. A 14% weight excess of Sm was used to compensate for the loss of Sm due to evaporation. The ingots were subsequently annealed for 1 week at 1000 °C, then hand crushed, and finally ball milled for 2.5 h to obtain fine powder with average grain size of about 5 μm. The resulting Sm_2Fe_{17} powder was nitrided in two stages: first, for 3 h at 250 °C, then for 5 h at 500 °C, under 0.8 bar of N_2.

The x-ray investigation of the obtained samples was carried out on a Philips diffractometer PW1820 using Co $K\alpha$ radiation. The lattice parameters were found to be as follows: $a = 8.558$ Å, $c = 12.448$ Å for Sm_2Fe_{17} and $a = 8.740$ Å, $c = 12.658$ Å for $Sm_2Fe_{17}N_x$. The nitrogen content x was determined from the intensities of the x-ray reflections ($x = 2.97 \pm 0.16$) and also by means of hot extraction ($x = 3.03 \pm 0.02$). The $Sm_2Fe_{17}N_x$ sample was found to contain about 11% of α-Fe.

The INS experiment was performed on the HET chopper spectrometer at ISIS in the UK. Powder samples, of mass 11–14 g, were wrapped in thin Al foil and mounted on the cold finger of a closed-cycle He refrigerator. The INS data for both the Sm_2Fe_{17} and $Sm_2Fe_{17}N_3$ samples were taken at $T = 20$ K. An incident neutron energy of 350 meV was chosen for Sm_2Fe_{17} and 250 meV for $Sm_2Fe_{17}N_3$. The chopper frequency was 550 Hz for Sm_2Fe_{17} and 600 Hz for $Sm_2Fe_{17}N_3$. This gave a full width at half maximum instrument resolution of 6.7 and 4.6 meV, respectively, for the two samples at an energy transfer of 170 meV.

The magnetization measurements were carried out in pulsed magnetic field up to 50 T at various fixed temperatures between 4.2 and 309 K. The rise time of the pulses was about 11 ms. A detailed description of the pulsed-field installation and pickup coil system has been published

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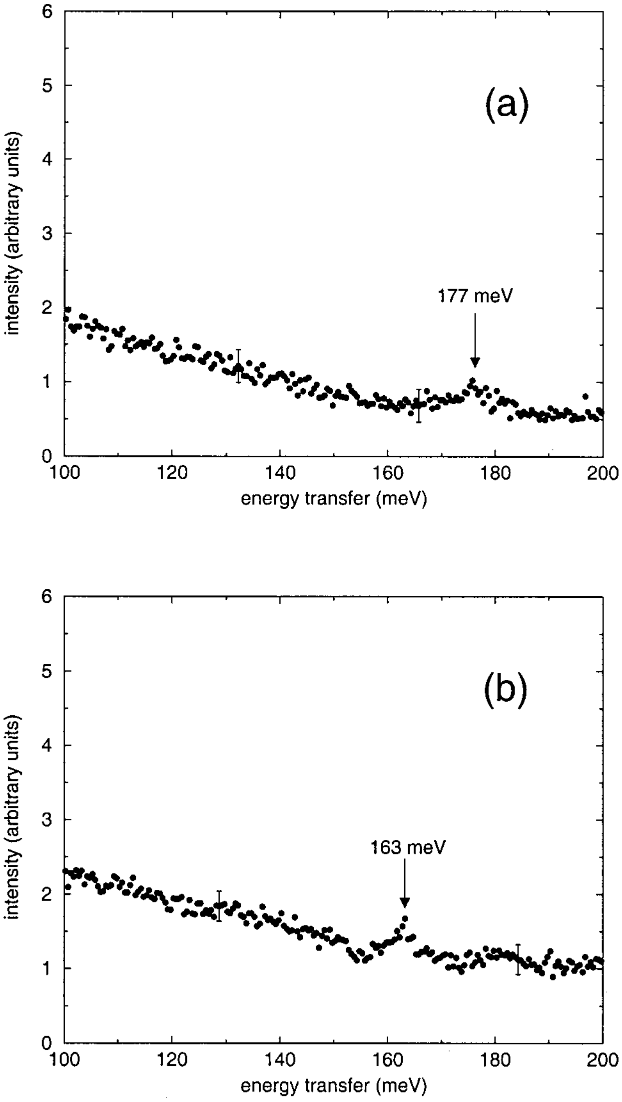

FIG. 1. Inelastic neutron spectra of (a) Sm_2Fe_{17} and (b) $Sm_2Fe_{17}N_3$, both at $T=20$ K, after background subtraction. The incident neutron energy was 350 meV for Sm_2Fe_{17} and 250 meV for $Sm_2Fe_{17}N_3$. The arrows indicate the positions of the peaks associated with the intermultiplet transition in Sm.

elsewhere.[3,4] The oriented powder sample for the magnetic measurements was prepared by compacting $Sm_2Fe_{17}N_3$ powder in a magnetic field of 2 T and then fixing it with epoxy resin. In the field range of up to 16 T the magnetization data were verified by measurements in an extraction magnetometer.

III. ANALYSIS OF THE INS DATA

The main feature of the INS spectra presented in Fig. 1 is the peak associated with the intermultiplet transition in samarium. In the nitride $Sm_2Fe_{17}N_3$ the peak is situated at $E_{\text{inter}}=163\,\text{meV}$, Fig. 1(b). This is to be compared with $E_{\text{inter}}=177\,\text{meV}$ in the parent compound, Fig. 1(a). The nitrogenation thus results in a clearly visible shift of the peak towards lower energies.

The observed decrease of E_{inter} is caused by the drop in the value of the exchange field B_{ex} experienced by the $4f$ shell of samarium. As demonstrated in the accompanying paper,[5] E_{inter} and B_{ex} are connected through the following simple relation:

$$\mu_B B_{\text{ex}}=\frac{63}{148}(E_{\text{inter}}-\Delta_{\text{so}})+\frac{26}{925}A_2^0\langle r^2\rangle, \tag{1}$$

where $\Delta_{\text{so}}=124\,\text{meV}$ is the spin-orbit splitting between the centers of gravity of the two lowest-J multiplets of Sm^{+3}.[6]

The last term in Eq. (1) is only a small correction, which in most cases is negligible and merely serves for error analysis. Thus A_2^0 in Sm_2Fe_{17} is known to be small, but neither its sign nor magnitude are known exactly. Putting $A_2^0\langle r^2\rangle=\pm 10\,\text{meV}$ in Eq. (1) simply produces an extra uncertainty of ± 5 T in B_{ex}. Since 10 meV is not an exact value, but rather a generously overestimated upper bound, one need not worry about having to transform A_2^0 from the crystallographic coordinates (with $\mathbf{z}\|[001]$) to the exchange field-related coordinates employed in Eq. (1), with $\mathbf{z}\perp[001]$. This transformation results in a factor of $-1/2$, already included in the estimate.

The main uncertainty in B_{ex} arises from the experimental error in determining the peak position E_{inter}. For Sm_2Fe_{17} we take $E_{\text{inter}}=176\pm 2$ meV, i.e., the average of our own value 177 meV [Fig. 1(a)] and the earlier result of Moze *et al.*,[7] 174.5 meV. Then Eq. (1) yields $B_{\text{ex}}=380\pm 30\,\text{T}$. (The error consists of ± 15 T coming from the uncertainty in E_{inter}, ± 5 T from A_2^0 and ± 10 T due to the neglect of J mixing.[5])

For the nitride we take $E_{\text{inter}}=163\pm 2\,\text{meV}$ [Fig. 1(b)] and $A_2^0\langle r^2\rangle=-30\pm 10\,\text{meV}$ (the latter estimate is inferred from the earlier results $A_2^0\langle r^2\rangle=-28\,\text{meV}$, as obtained by fitting high-field magnetization curves,[8] and $A_2^0\langle r^2\rangle=-34\,\text{meV}$, as found from low-field experiments[9]). Since $Sm_2Fe_{17}N_3$ is an easy-axis material, $\mathbf{B}_{\text{ex}}\|[001]$, no transformation of A_2^0 is required. Putting the values in Eq. (1) results in $B_{\text{ex}}=270\pm 30\,\text{T}$.

Comparing this value with the B_{ex} of the parent compound, one concludes that nitrogenation of Sm_2Fe_{17} leads to a 30% reduction in B_{ex}, in the same way as happens in the Gd_2Fe_{17} system.[2]

IV. ANALYSIS OF THE MAGNETIZATION DATA

The exchange field on samarium in $Sm_2Fe_{17}N_3$ has proved significantly weaker than assumed in the earlier work,[8] $B_{\text{ex}}=320\,\text{T}$ at $T=0$. This calls for a revision of the estimate of the leading crystal field parameter, $A_2^0=-28\,\text{meV}$, obtained in Ref. 8.

The analysis will be based primarily on our own magnetization data, which is advantageous from two points of view. First, the sample for our magnetic measurements was made from the same powder as the one employed in the INS experiments. Second, the higher magnetic field (up to 50 T) available in our pulsed-field installation ensures reliable saturation at room temperature, which was not achieved in the earlier experiments of Kato *et al.*[12]

Presented in Fig. 2 are the magnetization curves at the

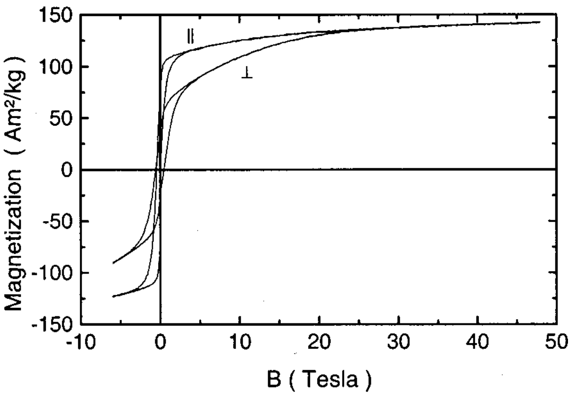

FIG. 2. Magnetization curves measured at $T = 309$ K on an orientated $Sm_2Fe_{17}N_3$ powder sample in a pulsed magnetic field directed along (∥) or across (⊥) the texture axis.

highest available temperature, $T = 309$ K, where the magnetic field was applied either along (∥) or across (⊥) the texture axis of the sample. The hysteresis, visible at $B < 4$ T, is indicative of domain wall motion phenomena, important in the low-field region. The curvature observed in the $M_\perp(B)$ dependence of Fig. 2 at intermediate fields (i.e., before saturation) should be attributed mainly to grain misalignment within the imperfectly textured sample, because the intrinsic curvature, proportional to the second anisotropy constant K_2, is already small at room temperature and rapidly decreases at higher temperatures—see Table II of Ref. 10. This was the main reason of concentrating on the high-temperature curves in our analysis.

The input data for the quantitative analysis are the spontaneous magnetization $M_s \approx 135\ \mathrm{A\,m^2/kg}$ and the anisotropy field $B_a \approx 23$ T, as determined from Fig. 2. The latter value agrees rather well with the earlier result $B_a \approx 19$ T obtained in low-field experiments.[10] Above room temperature one can use the approximate relation $K_1 = \frac{1}{2} M_s B_a$ to evaluate the first anisotropy constant. Therefore, at $T = 309$ K one has $K_1 = 1.55$ kJ/kg, or 11.9 MJ/m^3 (the conversion factor is the density, $\rho = 7.7 \times 10^3\ \mathrm{kg/m^3}$). The contribution to K_1 from the iron sublattice is negative and rather small. It can be taken from the measurements on the isomorphous $Y_2Fe_{17}N_3$ compound:[11] $K_1^{\mathrm{Fe}} = -1.1\ \mathrm{MJ/m^3}$ at $T = 300$ K. Thus for the samarium contribution one gets $K_1^{\mathrm{Sm}} = K_1 - K_1^{\mathrm{Fe}} = 13.0\ \mathrm{MJ/m^3}$, or 11.3 meV/Sm atom at $T = 309$ K.

The usefulness of knowing K_1^{Sm} is due to the fact that in the high-temperature regime ($\mu_B B_{\mathrm{ex}}/kT \ll 1$) it is directly proportional to the leading crystal field parameter A_2^0, despite the failure for $Sm_2Fe_{17}N_3$ of the standard linear approximation which requires the ratio $A_2^0\langle r^2\rangle/\mu_B B_{\mathrm{ex}}$ to be small.[8] In particular, for Sm compounds one has[13]

$$K_1^{\mathrm{Sm}} = -\alpha_J A_2^0 \langle r^2\rangle \left[18.75 B_{5/2}^{(2)}(x) + 36 \frac{\Delta_{\mathrm{ex}}}{\Delta_{\mathrm{so}}} B_{5/2}(x) \right], \quad (2)$$

where

$$B_{5/2}(x) = 1.2 \coth(1.2x) - 0.2 \coth(0.2x) \quad (3)$$

is the usual (first-order) Brillouin function for $J = 5/2$,

$$B_{5/2}^{(2)}(x) = 1.4 - 0.6 \coth(0.2x) B_{5/2}(x) \quad (4)$$

is the second-order generalized Brillouin function,

$$x = 2.5 \Delta_{\mathrm{ex}}/kT \quad (5)$$

is Langevin's magnetothermal ratio, and

$$\Delta_{\mathrm{ex}} = \frac{10}{7} \mu_B B_{\mathrm{ex}} \quad (6)$$

is the exchange (Zeeman) splitting between two adjacent levels of the ground multiplet of Sm^{3+}.

The first term in the square brackets of Eq. (2) arises within the standard single-ion model and describes the effect of the second-order crystal field on the ground ($J = 5/2$) multiplet of Sm^{3+}. It goes back to the original work of Yoshida[14] [cf. Eq. (4) and the expression in braces in Eq. (18) of Ref. 14].

The second term in Eq. (2) describes J mixing, important in Sm compounds. In essence, it is a second-order correction, bilinear in the crystal field and Sm-Fe exchange, which are both regarded as perturbations with respect to the spin-orbit coupling. Full details of the rather lengthy derivation[13] cannot be reproduced here for lack of space.

To estimate the product $A_2^0\langle r^2\rangle$, one needs to evaluate the square brackets of Eq. (2) at $T = 309$ K. To this end the low-temperature value of the exchange field, $B_{\mathrm{ex}} = 270$ T, should be scaled down by a factor of 0.93 [obtained through Eq. (16) of Ref. 8] resulting in $B_{\mathrm{ex}} = 250$ T at $T = 309$ K. Then, by virtue of Eqs. (6) and (5), $\Delta_{\mathrm{ex}} = 20.7$ meV and $x = 2.0$. The table on p. 147 of Ref. 15 contains the value $B_{5/2}(2.0) = 0.6935$, and in Table II of Ref. 16 one finds $B_{5/2}^{(2)}(2.0) = 0.3048$. Thus the square brackets of Eq. (2) evaluate to 9.74. Since for Sm^{3+} $\alpha_J = 13/315$, Eq. (2) becomes $K_1^{\mathrm{Sm}} = -0.40 A_2^0\langle r^2\rangle = 11.3$ meV. Hence $A_2^0\langle r^2\rangle = -28$ meV.

V. DISCUSSION

It has been established that the exchange field on Sm in the candidate permanent magnet material $Sm_2Fe_{17}N_3$ is some 30% lower than it is in the parent compound Sm_2Fe_{17}, $B_{\mathrm{ex}} = 270$ T vs 380 T at $T = 0$, respectively. This finding puts $Sm_2Fe_{17}N_3$ into the lower league of "under-300's" and casts serious doubt on its chances of becoming a champion of the permanent-magnet industry.

The drawback of low B_{ex} is partially offset by the extraordinarily strong crystal field, $A_2^0\langle r^2\rangle = -28$ meV. The combination of a very high A_2^0 with a mediocre B_{ex} in $Sm_2Fe_{17}N_3$ makes the failure of the usual linear theory of single-ion anisotropy even more spectacular than reported earlier.[8] The ratio $A_2^0\langle r^2\rangle/\mu_B B_{\mathrm{ex}}$, which is about -2 at room temperature, can hardly be regarded as a small parameter. However, the validity of our analysis, based upon Eq. (2), is uncompromised since it relies only on the smallness of $\mu_B B_{\mathrm{ex}}/kT \approx 0.54$ at $T = 309$ K.

The newly obtained estimate of the leading crystal field parameter, $A_2^0\langle r^2\rangle = -28$ meV, differs somewhat from the earlier value, -34 meV, deduced from low-field magnetization data.[9] Yet the agreement should be regarded as satisfactory, given that J mixing was neglected in Ref. 9.

Incidentally, the earlier analysis in Ref. 8 of the high-field magnetization data from Ref. 12 yielded the same result as the present work, $A_2^0\langle r^2\rangle = -28\,\mathrm{meV}$, even though a higher B_{ex} value was assumed in Ref. 8. This seems to disagree with our earlier assertion that precise knowledge of B_{ex} is important for unambiguous determination of A_2^0. The apparent contradiction is resolved, however, when one notes that the anisotropy field of the sample studied in the experiments of Kato *et al.*,[12] whose data were analyzed in Ref. 8, was also higher than the B_a of our sample. Namely, we get $B_a = 23\,\mathrm{T}$ at $T = 309\,\mathrm{K}$, whereas 26 T available to Kato *et al.* did not suffice to reach saturation at $T = 296\,\mathrm{K}$.[12]

The higher anisotropy field may be due to a higher nitrogen content x in the sample used by Kato *et al.* It is known that B_a is much enhanced in the $\mathrm{Sm_2Fe_{17}N}_x$ compounds with $x > 3$.[17] This increase of B_a may be attributed to either a further rise of A_2^0 above $x = 3$ or to a change of slope of the dependence $B_{\mathrm{ex}}(x)$ from negative below $x = 3$ to positive above that point, or to both effects simultaneously. INS experiments on $\mathrm{Sm_2Fe_{17}N}_x$ with $x > 3$ are therefore highly desirable.

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