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Magnetic properties of $Sm_2Fe_{17}N_x$, $x = 3.9$

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Abstract

Hydrogen decrepitation of Sm_2Fe_{17} followed by treatment in ammonia produces interstitial nitrides with nitrogen concentrations greater than three per formula unit. Measurements of the lattice parameters and magnetic properties are consistent with interstitial nitrogen occupation of the 9e and either the 3b or 18g sites. The effect of the extra nitrogen on the iron sublattice is to reduce the overall moment, particularly of the 18h sites. The magnetocrystalline anisotropy constants K_1 and K_2 indicate a significant decrease in the easy-axis character compared to $Sm_2Fe_{17}N_3$ material.

Keywords: RE–TM alloys – interstitial nitrides; Magnetocrystalline anisotropy; Mössbauer spectroscopy– RE–TM compounds

The incorporation of interstitial nitrogen in Sm_2Fe_{17} by reaction with molecular nitrogen or ammonia enhances the hard magnetic properties of the system [1,2]. The reactions with ammonia are more vigorous and under non-equilibrium conditions interstitial concentrations may exceed three nitrogen atoms per formula unit [3,4]. Here homogeneous samples having $x > 3$ are produced by a combination of hydrogen decrepitation and nitrogenation in ammonia. The magnetic properties are measured and the magnetocrystalline anisotropy constants K_1 and K_2 are deduced.

Samples were prepared from homogenised ingot materials supplied by Vacuumschmelze GmbH and the Santoku Co. Hydrogen decrepitation (HD) was used to reduce the ingot material to powder, suitable for nitrogenation. Preliminary treatment of the ingot material involved polishing the surface and vacuum treatment (10^{-5} mbar) at room temperature for up to 72 h [5]. The HD process conditions were 1 bar hydrogen at 300°C for 1 h. The hydrogen is interstitially incorporated into the intermetallic producing microcracks which in time reduce the particle size. Nitrogenation was conducted on the fully hydrided powders, using the same treatment developed to produce $Sm_2Fe_{17}N_3$ materials [6], i.e. a static ammonia atmosphere at 425°C for 6 h. The samples were cooled in vacuum to remove any hydrogen. The interstitial nitrogen concentration (x) was deduced from the weight gain after ammonia treatment. A composition of $Sm_2Fe_{17}N_{3.9}$ was obtained.

Powder X-ray diffraction, using Cu K_α radiation (λ = 1.54 Å), was used to measure the lattice parameters and unit cell volume, $a = 8.763 \pm 0.005$ Å, $c = 12.813 \pm 0.005$ Å, $c/a = 1.46$, and $V = 852.09$ Å^3. The anisotropic nature of the expansion, when $x > 3$, is illustrated in Fig. 1. Here the lattice parameters of the samples with interstitial nitrogen concentration from 0–3 [7] are combined with the $x = 3.9$ data. The c-axis shows a sharp increase at $x < 3$ whereas the a-axis shows little change. The anisotropic expansion indicates the presence of interstitial atoms along the c-axis, either on the 3b or some of the 18g sites. Curie temperature measurements were made using a thermobalance. The T_c of the $Sm_2Fe_{17}N_{3.9}$ material was 460 ± 5°C which is a decrease of 10°C compared to $Sm_2Fe_{17}N_3$ material. This results is consistent with interstitial nitrogen atoms not only in the ab-plane, as in $Sm_2Fe_{17}N_3$, but along the c-axis between the rare-earths. Occupation of such sites effects the strongly distance dependent 6c (4f) iron dumbbell atoms depressing the Curie temperature [8].

Magnetic measurements were conducted in Laboratoire Louis Néel, CNRS, Grenoble, using an extraction magnetometer in the temperature range 4.2 to 300 K and in fields up to 10 T. The powder samples were first aligned and fixed in epoxy resin in a 1 T field. Measurements were made in both the hard and easy directions. At 300 K, the magnetisation, measured in the easy direction, at 10 T was 128 J/Tkg. The magnetocrystalline anisotropy constants K_1 and K_2 were deduced from fitting the experimental data to the analytical expression based on [9],

$$\frac{\partial E}{\partial \phi} = 2K_1 \sin\phi\cos\phi + 4K_2 \sin^3\phi\cos\phi - HJ_s \int_\Omega f(\theta_0)\sin(\phi - \phi_0)\,d\Omega_0 = 0, \quad (1)$$

$$J = J_s \int_\Omega f(\theta_0)\cos(\phi_0 - \phi)\,d\Omega_0. \quad (2)$$

ϕ is the angle between J_s and the c-axis in the direction of (θ_0, φ_0) and $\phi_0 = \arccos(\sin\theta_0\cos\varphi_0)$, is the angle

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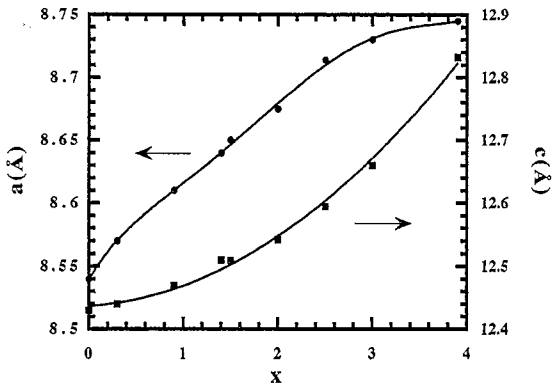

Fig. 1. Crystallographic lattice parameters a (●) and c (■) for $Sm_2Fe_{17}N_x$ ($x = 0$–3.9).

between the c-axis and the applied field, along the x-axis. The texture of the c-axis in the samples, $f(\theta_0)$, was assumed to have a Gaussian distribution. Results of the temperature dependence of K_1 and K_2 are plotted in Fig. 2. The K_1 contribution decreases continuously but the K_2 contribution has a maximum at 150 K. The magnitude of K_1 shows a significant drop compared to the $x = 3$, e.g. at 300 K $K_1 = 8.7$ MJ/m^3 for $x = 3$, but for $x = 3.9$ $K_1 = 1.35$ MJ/m^3. The anisotropy field calculated for the $Sm_2Fe_{17}N_{3.9}$ sample, $\mu_0 H_a = (2K_1 + 4K_2)/M_s$ at 300 K is 5.6 T, compared to 19 T for $x = 3$.

Mössbauer measurements were made at room temperature with 10–15 mCi, ^{57}corhodium source. Calibration was carried out using an α-Fe absorber. The spectra were fitted assuming an intensity ratio of 6:9:18:18 which corresponds to 6c, 9d, 18h, 18f sites, respectively. Assuming some interstitial atoms occupy the 3b or 18g sites, the 18h site was split into two subspectra representing iron sites with or without nitrogen neighbours. The average B_{hf} and IS for $x = 3.9$ are shown together with results for samples $x = 0$–3 [7], (Fig. 3). The average isomer shift increases monotonically with increasing x. For $x > 3$ the average hyperfine field decreases sharply, relative to $Sm_2Fe_{17}N_3$, in agreement with the decrease in magnetisation observed

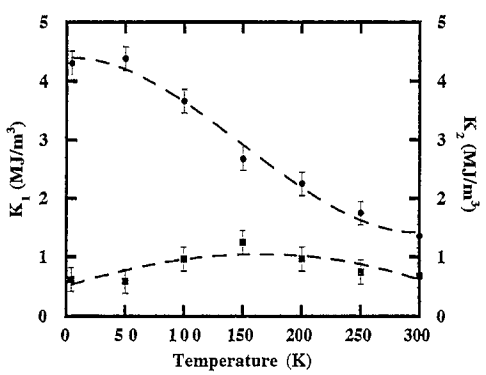

Fig. 2. Temperature dependence of the magnetocrystalline anisotropy constants K_1 (●) and K_2 (■) for $Sm_2Fe_{17}N_{3.9}$.

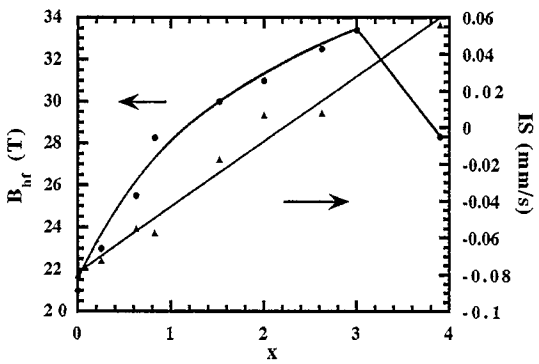

Fig. 3. Average hyperfine field (●) and isomer shift (▲) for $Sm_2Fe_{17}N_x$ ($x = 0$–3.9).

in magnetic measurements. The strongest effect is observed at the 18h site where a sharply reduced moment and increased isomer shift are consistent with a tendency to form covalent bonds with nitrogen. The hybridised 4s–3d orbitals reduces the 4s electron density and increases the occupation of the 3d ↓ orbitals.

Hydrogen pretreatment influences the metastable state of the $Sm_2Fe_{17}N_x$ system. Results from powder X-ray diffraction, Curie temperature, Mössbauer and magnetisation measurements for $Sm_2Fe_{17}N_{3.9}$ material are consistent with interstitial nitrogen filling the 9e and either the 3b or some 18g sites. Interstitial nitrogen on the non-9e sites strongly influence the 18h iron atoms, reducing the overall magnetic moment. The sharp decrease in the value of the magnetocrystalline anisotropy constant K_1 reflects how interstitial nitrogen atoms situated along the c-axis drastically reduce the easy-axis character of the material.

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