Magnetic structure of NdScGe

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We have determined the magnetic structure of NdScGe (tetragonal $I4/mmm$) by high-resolution neutron powder diffraction, ac-susceptibility and magnetometry. The magnetic ordering temperature is 194(2) K and the magnetic structure is characterized by ferromagnetic order of the Nd sublattice, lying in or close to the tetragonal basal plane. The Nd moment at 4 K is 3.2(2) μ_B and, in contrast to the claims of a recent Perturbed Angular Correlation study, we find no evidence for a lattice softening effect suggested to occur around the Curie temperature. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1851884]

I. INTRODUCTION

The intermetallic compound NdScGe forms as an ordered variant of the tetragonal La_2Sb structure (Pearson symbol tI12). The space group is $I4/mmm$ (#139) and there are four formula units per tetragonal cell. The site occupancies are $4e_1$ for Nd, $4e_2$ for Ge, generated by $(0\ 0\ z)$, and $4c$ for Sc, generated by $(0\frac{1}{2}0)$.

Recently, Mishra and Dhar[1] reported a Perturbed Angular Correlation (PAC) study of NdScGe using ^{111}In doping. The In/Cd probe occupies the Sc site and these authors reported an unusual temperature dependence of the quadrupole frequency which they interpreted as evidence of a softening of the lattice occurring around the Curie temperature of 200 K.[2] The magnetic structure of NdScGe was reported to be a ferromagnet and, by fitting the PAC data to a combination of hyperfine magnetic and electric quadrupole effects, Mishra and Dhar deduced an angle β of 45(3)° between the transferred hyperfine magnetic field at the probe site (from the magnetic Nd sublattice) and the principal Z-axis of the electric field gradient (EFG) at the ^{111}In/Sc site; the EFG Z-axis was assumed to lie along the tetragonal C-axis [001]. Thus, the magnetic order of the Nd sublattice at 25 K was suggested to be ferromagnetic and canted away from the tetragonal C-axis by 45(3)°. Furthermore, Mishra and Dhar used magnetization data to deduce a Nd moment at 10 K of only 2.0 μ_B, greatly reduced from the Nd^{3+} "free-ion" value of 3.27 μ_B.

In this paper we present a determination of the magnetic structure of NdScGe using high-resolution neutron powder diffraction, complemented by ac-susceptibility and magnetometry.

II. EXPERIMENTAL METHODS

The NdScGe sample was prepared by arc-melting stoichiometric amounts of the pure elements (at least 3N) under Ti-gettered argon. The arc-melted ingot was annealed *in vacuo* at 1050 °C for 2 weeks. Powder x-ray diffraction employed Cu-K_α radiation on an automated Nicolet–Stoe diffractometer. ac-susceptibility (398 A/m RMS and 137 Hz) and magnetometry measurements were made on a Quantum Design PPMS.

Neutron powder diffraction experiments were carried out on the DUALSPEC C2 high-resolution diffractometer at the NRU reactor, Chalk River Laboratories, operated by Atomic Energy Canada Ltd. The neutron wavelength was 1.3285(1) Å. Eight diffraction patterns were obtained over the temperature range 4–250 K and all patterns were analyzed using the Rietveld method and the FULLPROF/WINPLOTR program.[3]

III. RESULTS AND DISCUSSION

The annealed sample of NdScGe was single-phase within the resolution of the x-ray and neutron powder diffraction experiments. In Fig. 1 we show the temperature dependence of the low-field magnetization of NdScGe. The ferromagnetic ordering temperature is 194(2) K.
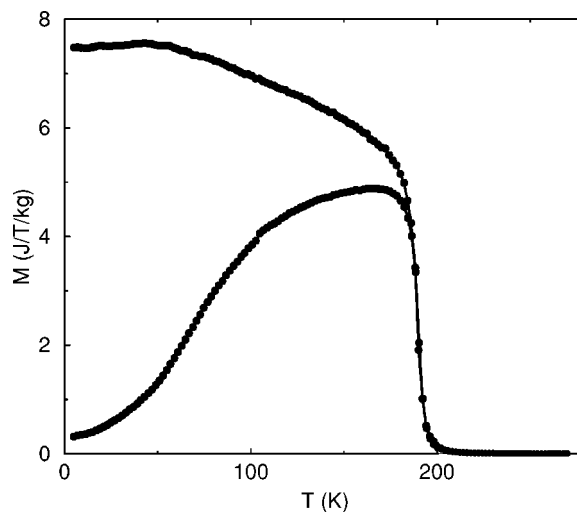

FIG. 1. Temperature dependence of the low-field ($B_{applied}=10$ mT) magnetization of NdScGe, measured in both field-cooled and zero-field-cooled modes.
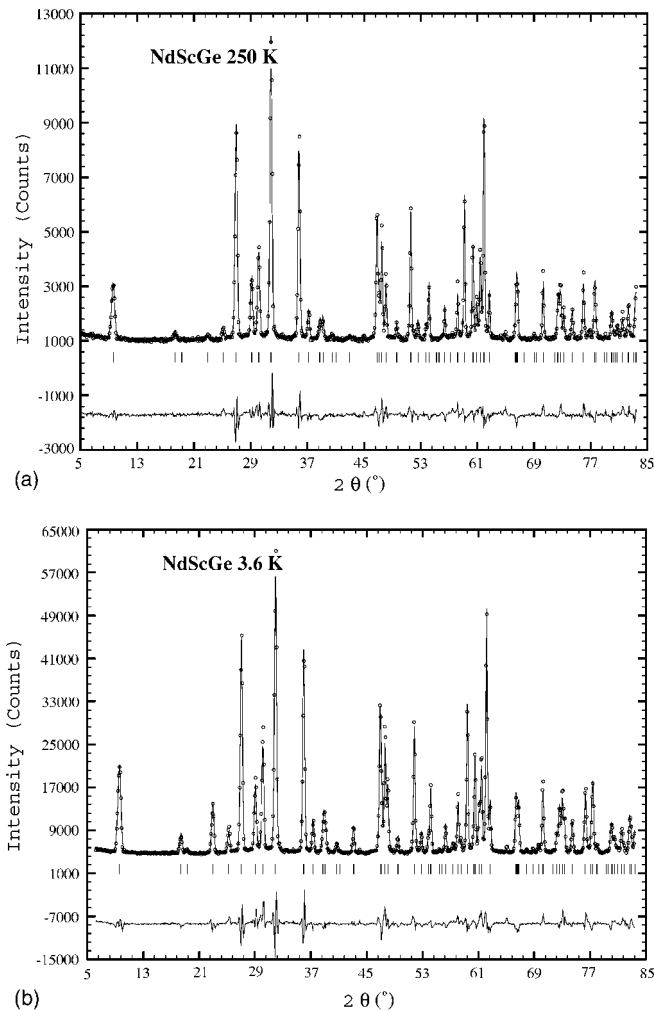
FIG. 2. Neutron powder diffraction patterns of NdScGe obtained at 250 K (top) and 4 K (bottom).

FIG. 3. Temperature dependencies of the lattice parameters of NdScGe. The full lines are visual guides.

The magnetization temperature dependences shown in Fig. 1 are indicative of significant coercivity in NdScGe, as seen in previous studies[1,2] [we measured a coercivity of 210(5) mT at 5 K]. The saturation magnetization is 52(1) J T^{-1} kg^{-1} at 5 K in an applied field of 9 T, which converts to a Nd magnetic moment of 2.43(5) μ_B, significantly lower than the free-ion value of 3.27 μ_B. This reduction in moment is most likely a consequence of the appreciable coercivity, although crystal-field quenching may also play a role.

In Fig. 2 (top) we show the neutron diffraction pattern of NdScGe obtained at 250 K i.e., in the paramagnetic regime. The z atomic position parameters for the Nd and Ge sites at 250 K are 0.3235(1) and 0.1235(1), respectively. The refinement R-factors (%) are $R(\text{Bragg})=6.3$ and $R(F\text{-structure})=4.6$.

In Fig. 2 (bottom) we show the neutron diffraction pattern of NdScGe obtained at 4 K i.e., in the ferromagnetic regime. The magnetic contribution to the overall scattering is most clearly evident in the (002) peak situated at $2\theta \sim 9.6°$ and the (103) peak at $2\theta \sim 23.0°$. The observation of a significant magnetic contribution to the (002) peak at 4 K ($\sim 25\%$ of total intensity) indicates that the Nd magnetic mo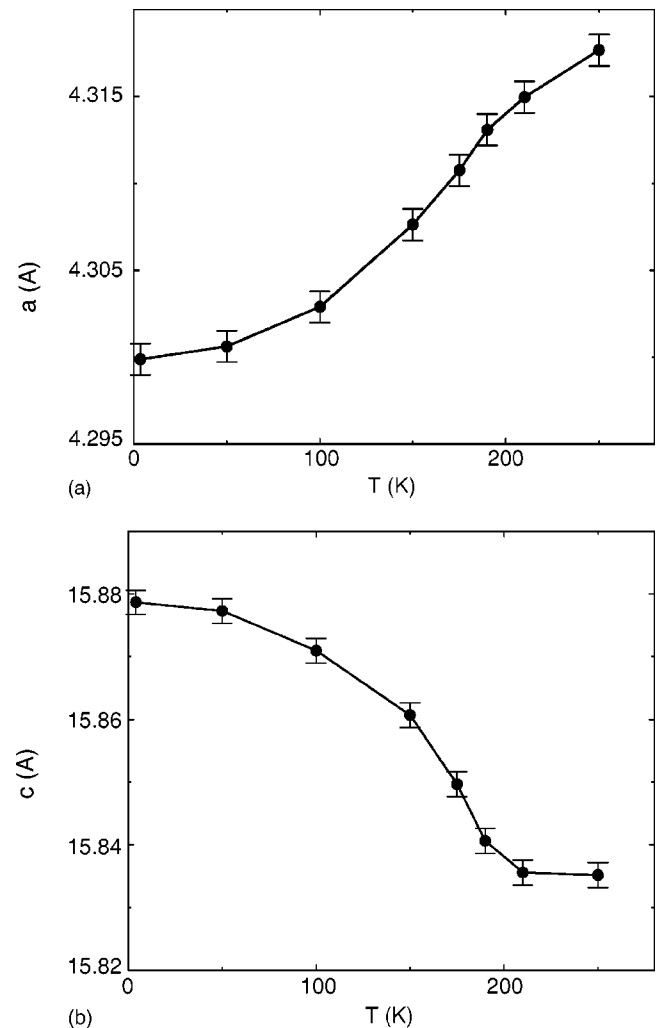ments cannot be aligned along the crystal C-axis at 4 K. Our refinement of the 4 K pattern shows that the magnetic structure is ferromagnetic with a Nd magnetic moment of 3.2(2) μ_B lying in or close to (within $\sim 15°$) the tetragonal basal plane. We note that the Nd magnetic moment determined by neutron diffraction attains the "free-ion" value. The refinement R-factors (%) are $R(\text{Bragg})=5.6$ and $R(F\text{-structure})=3.7$.

In Fig. 3 we show the temperature dependencies of the a and c lattice parameters. The unusual temperature dependence of the c parameter, increasing with decreasing temperature, suggests a magnetostrictive effect driven by the magnetic ordering of the Nd sublattice. Such behaviour has also been observed in TbFeSi and DyFeSi by Welter *et al.*[4] (these RFeSi compounds crystallize in the related tetragonal CeFeSi-type $P4/nmm$ structure; $P4/nmm$ is a Type IIA maximal nonisomorphic subgroup of the $I4/mmm$ group of NdScGe).

In Fig. 4 we show the temperature dependence of the overall isotropic thermal parameter deduced from the refinement of the neutron diffraction patterns. These data show no anomalous behavior around the Curie temperature 194(2) K which one might expect to observe if a lattice softening were to occur around the Curie temperature.
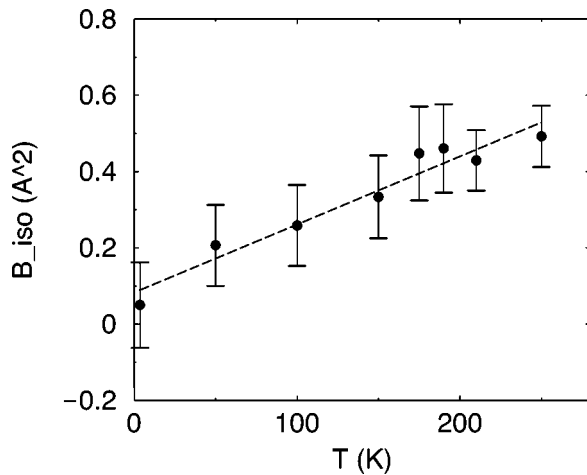
FIG. 4. Temperature dependence of the overall isotropic thermal parameter of NdScGe. The dotted line is a linear fit to these data and is included purely as a visual guide.

In the analysis of the PAC study by Mishra and Dhar,[1] an angle of $\beta = 45(3)°$ between the transferred hyperfine magnetic field at the Sc site from the Nd sublattice and the Z-axis of the electric field gradient at the Sc site was deduced. The point symmetry of the Sc 4c site in NdScGe is (m mm ·) which means that the XYZ principal axis frame of the electric field gradient is coincident with the crystal ABC axes and Mishra and Dhar assumed the Z-axis to be the crystal C-axis, although one cannot identify specifically the individual EFG axes *a priori*.

There are a number of problems involved with trying to reconcile the neutron diffraction and PAC data with a view to determining the magnetic order of the Nd sublattice in Nd-ScGe. First of all, the PAC technique is only sensitive to the *magnitude* of the electric quadrupole term in the nuclear Hamiltonian, limiting the range of angles that can be uniquely determined. Second, one must consider the *specific* identification of the EFG axes. If the Z axis of the EFG lies along the crystal A-axis [100] rather than the C-axis as assumed by Mishra and Dhar,[1] then our deduced Nd sublattice magnetization planar orientation leads to an angle β of 45°, in full agreement with the PAC angle of 45(3)°. Here, we assume that the basal plane orientation of the Nd moment is along [110]; unfortunately, one cannot determine the exact planar orientation of the Nd moment, [100] or [110], by powder diffraction on a tetragonal space group.[5]

Finally, the severe damping of the PAC signal that occurs as the magnetic order develops below T_c, greatly limits the information that can be extracted from the data. The energy splittings induced by the EFG and hyperfine field (B_{hf}) are of comparable magnitudes even at the lowest temperature studied [25 K (Ref. 1)] so that the commonly used assumption that the nuclear electric quadrupole interaction can be treated as a perturbation on the hyperfine magnetic interaction is always invalid in this system. A full solution to the nuclear Hamiltonian must be used to calculate the expected PAC patterns. Comparison of full-solution PAC spectra calculated using a fixed value for the EFG (we used the 296 K value which is well determined) with patterns calculated using the temperature dependent values[1] reveals that differences are apparent only at relatively late times ($t > 70$ ns) where the severe damping of the observed signal leaves it dominated by counting statistics. Reliable extraction of hyperfine parameters in this situation would be extremely difficult.

In conclusion, our neutron diffraction data are in complete agreement with the PAC angle of 45(3)° between the EFG and magnetization axes, *if* we take the magnetization axis as [100] rather than [100]. However, we find no evidence for lattice softening or distortions at T_c and believe that the previous claim for this behavior is incorrect, resulting from limitations of the PAC technique and data.

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