The magnetic structure of Nd$_5$Sn$_4$

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Nd$_5$Sn$_4$ adopts the orthorhombic $Pnma$ structure, and orders antiferromagnetically below 36(3) K. The neutron diffraction pattern at 4 K reveals that the magnetic space group is $Pn'm'a'$, a complex canted-antiferromagnetic structure. The Nd 4c magnetic mode is $A_2C_2$ and the Nd 8d magnetic mode is $A_2^0G_7C_6$. The Nd magnetic moments are 1.76(8), 2.44(12), and 2.63(10)$\mu_B$ at 4c, 8d$_1$, and 8d$_2$ sites, respectively. These results are in agreement with our Mössbauer spectroscopy and magnetic measurements. © 2005 American Institute of Physics. DOI: 10.1063/1.1850253

I. INTRODUCTION

Interest in magnetocaloric materials was rekindled by the discovery of the near room temperature giant magnetocaloric (GMC) effect in Gd$_5$Si$_{4-x}$Ge$_{x-1}$.

II. EXPERIMENTAL METHODS

Nd$_5$Sn$_4$ was prepared in a tri-arc furnace with a base pressure of $6 \times 10^{-7}$ mbar. Stoichiometric amounts of Nd (99.9 wt %, purchased from Alfa Aesar) and Sn (99.99 wt %) were melted under pure argon. To ensure homogeneity, the alloys were remelted several times. The alloy was air-sensitive, so all sample handling was performed in a glove box under a pure argon atmosphere.

The ac susceptibility (0.5 mT at 137 Hz) and magnetization (in fields up to 9 T) were measured using a commercial Quantum Design extraction magnetometer. 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 diffraction data at 295 K with wavelength 1.32978(8)Å were collected between 5° and 117° of 2θ in two banks by moving the detector to permit accurate determination of the atomic thermal parameters during the structural refinement. Low temperature data at 4, 55, and 80 K with wavelength 2.3688(6)Å were collected between 3° and 83° of 2θ in one bank. All diffraction patterns were refined by the Rietveld method using the GSAS program. Mössbauer spectra were collected using a 74 MBq $^{119}$Sn BaSnO$_3$ source. The system was calibrated using $\alpha$-Fe and a $^{57}$Co source. The temperature was varied from 10 to 295 K using a vibration-isolated closed-cycle refrigerator.

III. RESULTS AND DISCUSSION

Analysis of the neutron diffraction pattern indicates that Nd$_5$Sn$_4$ adopts the orthorhombic $Pnma$ Sm$_3$Ge$_4$-type (O(II)) structure at 295 K, with $a=8.2093(6)$Å, $b=15.8504(13)$Å, and $c=8.3797(7)$Å, in good agreement with earlier XRD results. About 9 wt % Nd$_{11}$Sn$_{10}$ and 4 wt % Nd$_5$Sn$_3$ were present as impurity phases, and were included in all pattern refinements reported here. No structural changes were detected between 4 and 295 K.

ac susceptibility reveals two magnetic transitions at 36(3) and 74(2) K, corresponding to Nd$_5$Sn$_4$ and Nd$_5$Sn$_3$ respectively. At 38 K, the Néel temperature of Nd$_5$Sn$_3$ (Ref. 13) is too close to that of Nd$_5$Sn$_4$ to be resolved. The magnetization curve at 5 K in Fig. 1 is far from saturation even in 9 T, and the break at 5 T is likely due to...
some form of spin-flop event. The rather small zero-field moment of \( -0.2\mu_B/\text{Nd} \) apparent in Fig. 1 is due to the ferromagnetic Nd\(_{11}\)Sn\(_{10}\) impurity which has a saturation moment of 1.26\( \mu_B/\text{Nd} \) at 5 K, suggesting that about 16 wt % is present in the Nd\(_5\)Sn\(_4\) sample, consistent with 9% estimated from neutron diffraction data. All these results are confirmed in the following using both neutron diffraction and \(^{119}\)Sn Mössbauer spectroscopy.

Figure 2 shows the neutron diffraction pattern of Nd\(_5\)Sn\(_4\) at 4 K. A high-intensity magnetic (010) peak at \(2\theta \sim 8.6^\circ\), which dominates the entire diffraction pattern, is clearly observed. Temperature dependence of (010) magnetic intensity (upper panel of Fig. 3) shows \( T_N \) at 38.7(1) K, in agreement with our ac susceptibility data. The magnetic contributions of the Nd\(_{11}\)Sn\(_{10}\) and Nd\(_5\)Sn\(_3\) impurities were not included in the magnetic fitting.

A complete analysis of magnetic space groups and allowed ordering modes has been presented earlier in our study of the isostructural Nd\(_5\)Ge\(_4\).\(^{14}\) Of the eight possible magnetic space groups associated with \( \text{Pnma} \), the best fit to the neutron pattern of Nd\(_5\)Sn\(_4\) at 4 K was obtained with the \( \Gamma_1 \) representation, corresponding to the magnetic space group \( \text{Pn}^{m'm'a'} \) with \( A_1C_1 \) and \( A_2^G C_2 \) antiferromagnetic modes for the 4c and 8d sites, respectively. The refinement \( R \)—factors for the best fit are: \( R(\text{Bragg and mag}) = 3.8\% \) and \( R(F) = 3.4\% \).

The lattice parameters (4 K) are \( a=8.2012(6)\text{Å} \), \( b=15.7830(13)\text{Å} \), and \( c=8.3354(6)\text{Å} \), and other refined parameters are given in Table I. The average Nd magnetic moment in Nd\(_5\)Sn\(_4\) is 2.38(10)\( \mu_B \). The Nd magnetic moments for the three sites are less than the free ion Nd moment of 3.27\( \mu_B \). This is probably due to crystal field effects.

The \(^{119}\)Sn Mössbauer spectrum of Nd\(_5\)Sn\(_4\) at 10 K [Fig. 3 (bottom)] is dominated by two magnetic components. One, with a magnetic hyperfine field of 9.63(2) T is well resolved, while the second, with a hyperfine field of 2.95(2) T presents as a doublet. Sn is nonmagnetic and so any hyperfine magnetic field observed at the \(^{119}\)Sn nucleus is due to the surrounding Nd magnetic moments. The orthorhombic structure of Nd\(_5\)Sn\(_4\) has three Sn sites: 4c, 4c\(_2\) and 8d and three Nd sites: 4c, 8d\(_1\) and 8d\(_2\). Sn atoms at the two 4c sites have 8 Nd nearest neighbors compared to 7 Nd atoms for the 8d site. Because of symmetry, the hyperfine fields at the two 4c sites are expected to be similar in Mössbauer spectroscopy study, and hence the three Sn sites divide into two equal groups: the
two 4c sites and the 8d site. The area ratio of the two magnetic subspectra is 1.2(1):1, consistent with the expected 1:1 for Sn in the (4c1+4c2)·8d sites. In addition, there is a Gaussian-broadened magnetic component with an average hyperfine field of 11.3(1) T corresponding to the Nd₄Sn₁₀ impurity phase. A weak nonmagnetic component is also observed.

There is no evidence of a structural transition in the Mössbauer data over the temperature range where magnetic order is present (10−80 K), consistent with our neutron diffraction results. The hyperfine fields of the two sharp magnetic sextets track together (middle panel of Fig. 3) and fall smoothly to zero at the the magnetic ordering temperature of Nd₄Sn₄ (≈37 K). The Gaussian-broadened magnetic component disappears between 70 and 80 K, in agreement with its assignment to the Nd₁₁Sn₁₀ impurity phase.

### IV. CONCLUSIONS

Nd₄Sn₄ crystallizes in the orthorhombic Pnma Sm₂Ge₂-type structure, and forms a complex canted antiferromagnetic structure with magnetic space group Pn′m′a′ corresponding to the Γ⁻¹ representation below a Néel temperature 36(3) K. Analysis of the neutron diffraction pattern at 4 K reveals that the average Nd magnetic moment is 2.38(10) μ₉, and the magnetic moments are essentially confined to the ac plane. No temperature induced structural transitions are found by neutron diffraction or Mössbauer spectroscopy.

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