The magnetic structure of Nd_5Sn_4

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Nd_5Sn_4 adopts the orthorhombic P*nma* structure, and orders antiferromagnetically below 36(3) K. The neutron diffraction pattern at 4 K reveals that the magnetic space group is P$n'm'a'$, a complex canted-antiferromagnetic structure. The Nd 4*c* magnetic mode is A_xC_z, and the Nd 8*d* magnetic mode is $A_x^-G_y^-C_z^-$. The Nd magnetic moments are 1.76(8), 2.44(12), and 2.63(10)μ_B at 4*c*, $8d_1$, 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 $Gd_5Si_xGe_{4-x}$.[1] The GMC effect is the result of a first-order magnetostructural transition. Therefore, understanding this complex interaction between structure and magnetic transitions is central to the study of the GMC effect. However, the high neutron absorption cross section of natural gadolinium limits direct determination of magnetic and crystal structures for $Gd_5Si_xGe_{4-x}$ compounds. Thus, GMC studies have expanded to other $R_5Si_xGe_{4-x}$ pseudobinary systems (R is a rare earth element),[2–4] where neutron diffraction can be used to characterize the magnetic structure. An alternative approach is to substitute Ge by Sn and use ^{119}Sn Mössbauer spectroscopy to study the magnetic and chemical environment of each crystallographically inequivalent Sn atom. This led to the study of $Gd_5Si_xSn_{4-x}$,[5] the discovery of the giant magnetocaloric material Gd_5Sn_4 (Ref. 6) and the observation of a first-order magnetostructural transition in Gd_5Sn_4 and $Gd_5Si_{0.4}Sn_{3.6}$.[7] Based on the motivation of using both neutron diffraction and Mössbauer spectroscopy techniques, the basic structural and magnetic properties of the $Nd_5Si_xSn_{4-x}$ system was recently reported.[8]

In this paper we describe the magnetic structure of Nd_5Sn_4 obtained from the analysis of diffractometry as a part of our work $Nd_5Si_xSn_{4-x}$.

II. EXPERIMENTAL METHODS

Nd_5Sn_4 was prepared in a tri-arc furnace with a base pressure of 6×10^{-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 1.329 78(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.[9] Mössbauer spectra were collected using a 74 MBq ^{119m}Sn $BaSnO_3$ source. The system was calibrated using α-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_5Sn_4 adopts the orthorhombic P*nma* Sm_5Ge_4-type (O(II)[10,11]) 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.[8] About 9 wt % $Nd_{11}Sn_{10}$ and 4 wt % Nd_5Sn_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_5Sn_4 and $Nd_{11}Sn_{10}$,[8,12] respectively. At 38 K, the Néel temperature of Nd_5Sn_3 (Ref. 13) is too close to that of Nd_5Sn_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

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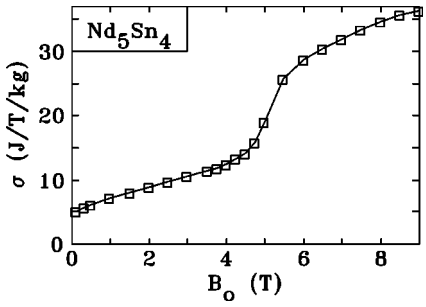

FIG. 1. Magnetization of Nd_5Sn_4 at 5 K.

some form of spin-flop event. The rather small zero-field moment of $\sim 0.2\mu_B$/Nd apparent in Fig. 1 is due to the ferromagnetic $Nd_{11}Sn_{10}$ impurity which has a saturation moment of $1.26\mu_B$/Nd at 5 K, suggesting that about 16 wt % is present in the Nd_5Sn_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_5Sn_4 at 4 K. A high-intensity magnetic (010) peak at $2\theta \sim 8.6°$, 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_5Sn_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_5Ge_4.[14] Of the eight possible magnetic space groups associated with P*nma*, the best fit to the neutron pattern of Nd_5Sn_4 at 4 K was obtained with the Γ_1^- representation, corresponding to the magnetic space group $Pn'm'a'$ with A_xC_z and $A_x^-G_y^-C_z^-$ antiferromagnetic modes for the 4*c* and 8*d* sites, respectively. The refinement R—factors for the best fit are: R(Bragg and mag)=3.8% and R(F)=3.4%. The lattice parameters (4 K) are $a=8.2012(6)$Å, $b=15.7830(13)$Å, and $c=8.3354(6)$Å, and other refined parameters are given in Table I. The average Nd magnetic moment in Nd_5Sn_4 is $2.38(10)\mu_B$. The Nd magnetic moments

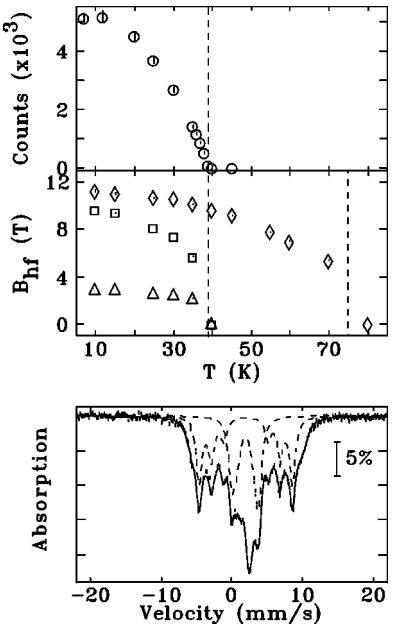

FIG. 3. Bottom:^{119}Sn Mössbauer spectrum of Nd_5Sn_4 at 10 K. The dashed lines indicate the two sharp sextets associated with Nd_5Sn_4 (see the text). Middle: Temperature dependence of the hyperfine fields for the sharp (△ and □) components due to Nd_5Sn_4 and Gaussian-broadened (◇) component attributed to $Nd_{11}Sn_{10}$. Top: Temperature variation of the (010) magnetic peak intensity seen at ~8.6° in Fig. 2

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_5Sn_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_5Sn_4 has three Sn sites: $4c_1$, $4c_2$ and 8*d* and three Nd sites: 4*c*, $8d_1$ and $8d_2$. Sn atoms at the two 4*c* sites have 8 Nd nearest neighbors compared to 7 Nd atoms for the 8*d* site. Because of symmetry, the hyperfine fields at the two 4*c* sites are expected to be similar in Mössbauer spectroscopy study, and hence the three Sn sites divide into two equal groups: the

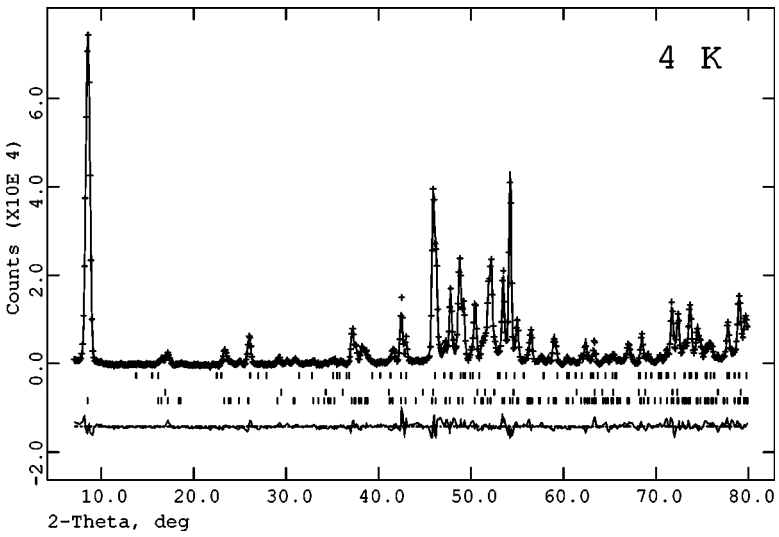

FIG. 2. Neutron diffraction pattern of Nd_5Sn_4 at 4 K. The Bragg markers (from top to bottom) are $Nd_{11}Sn_{10}$, Nd_5Sn_3, and Nd_5Sn_4 (nuclear and magnetic). Solid line below markers shows residuals.

TABLE I. Refined structural and magnetic parameters for Nd_5Sn_4 at 4 K.

Atom	x/a $M_x(\mu_B)$	y/b $M_y(\mu_B)$	z/c $M_z(\mu_B)$	$M(\mu_B)$
Nd1 (4*c*)	0.300(2)	0.25	0.009(2)	
	1.73(7)	0	−0.28(17)	1.76(8)
Nd2 (8*d*)	0.1320(13)	0.1209(6)	0.3360(12)	
	2.06(10)	0.3(2)	1.28(11)	2.44(12)
Nd3 (8*d*)	0.9883(14)	0.0972(8)	0.8169(15)	
	2.20(9)	0.86(13)	−1.16(11)	2.63(10)
Sn1 (4*c*)	0.930(3)	0.25	0.1119(19)	
Sn2 (4*c*)	0.182(2)	0.25	0.642(3)	
Sn3 (8*d*)	0.2149(19)	0.9538(9)	0.5214(19)	

two 4*c* sites and the 8*d* site. The area ratio of the two magnetic subspectra is 1.2(1):1, consistent with the expected 1:1 for Sn in the $(4c_1+4c_2):8d$ sites. In addition, there is a Gaussian-broadened magnetic component with an average hyperfine field of 11.3(1) T corresponding to the $Nd_{11}Sn_{10}$ 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 Nd_5Sn_4 (~37 K). The Gaussian-broadened magnetic component disappears between 70 and 80 K, in agreement with its assignment to the $Nd_{11}Sn_{10}$ impurity phase.

IV. CONCLUSIONS

Nd_5Sn_4 crystallizes in the orthorhombic P*nma* Sm_5Ge_4-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) μ_B, 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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