Magnetic properties of $Nd_5Si_xSn_{4-x}$

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The structure and magnetic properties of $Nd_5Si_xSn_{4-x}$ have been investigated using x-ray diffraction, ^{119}Sn Mössbauer spectroscopy and bulk magnetic techniques. The crystal structure is orthorhombic for $x \leqslant 3.5$, above which it is tetragonal. The ac-susceptibility shows that the magnetic ordering temperatures of $Nd_5Si_xSn_{4-x}$ increase from 35 to 120 K as x increases. Magnetization data indicate that the Nd moments cannot be ordered ferromagnetically at 5 K and that the magnetic structure must be mixed ferro-antiferromagnetic form as seen in the $Nd_5Si_xGe_{4-x}$ system. The ^{119}Sn Mössbauer spectra of $Nd_5Si_xSn_{4-x}$ at 9 K are dominated by two, sharp hyperfine sextets with fields between 10 and 16 T that increase with x. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Interest in magnetocaloric materials has been rekindled by the discovery of the giant magnetocaloric effect in $Gd_5Si_xGe_{4-x}$.[1] The structural and magnetic phase diagrams have been established[2,3] and the magnetocaloric effect has been associated with coupled magnetic and structural transitions. Understanding this complex interaction between structure and magnetic order is central to the study of the giant magnetocaloric effect. The high neutron absorption cross section of natural Gd makes it effectively impossible to study the $Gd_5Si_xGe_{4-x}$ system with conventional neutron scattering techniques. One must therefore use isotopically separated Gd, change to another rare earth, or find an alternative characterization technique. While the first approach has yet to be tried, the $Nd_5Si_xGe_{4-x}$ system has been studied extensively, with both its crystal structure[4] and magnetic structure[5] being reported. ^{119}Sn Mössbauer spectroscopy has also emerged as an alternative characterization technique since Sn substitutes well for either Si or Ge, and Mössbauer spectroscopy can be used to obtain both structural and magnetic information. The $Gd_5Si_xSn_{4-x}$ system has been characterized,[6] and more recently, the field and temperature driven first order magnetic and structural transition in Gd_5Sn_4 has been investigated using ^{119}Sn Mössbauer spectroscopy.[7] By moving to the $Nd_5Si_xSn_{4-x}$ system, which can be studied by both ^{119}Sn Mössbauer spectroscopy and conventional neutron scattering techniques, we hope to correlate the information obtained and in doing so extend our understanding of magnetic ordering in the $Gd_5Si_xSn_{4-x}$ system, which is inaccessible by neutron diffraction.

We report here a preliminary study of the structural and magnetic properties of the $Nd_5Si_xSn_{4-x}$ system using x-ray diffraction, susceptibility, magnetization, and ^{119}Sn Mössbauer spectroscopy. The structural behavior is simpler than that of the $Nd_5Si_xGe_{4-x}$ system, where a monoclinic form was found at intermediate germanium contents, while magnetic measurements suggest that the present system also exhibits the complex magnetic structures reported for Nd_5Si_4 and Nd_5Ge_4.[5] We found no evidence of a giant magnetocaloric effect in any of the alloys studied in this system.

II. EXPERIMENTAL METHODS

The $Nd_5Si_xSn_{4-x}$ samples were prepared in a tri-arc furnace with a base pressure of 6×10^{-7} mbar. Stoichiometric amounts of Nd (99.9%), Si (99.99%), and Sn (99.99%) were melted under Ti-gettered argon. To ensure homogeneity, the alloys were inverted and remelted several times. Tin-rich samples were found to be air sensitive, therefore all sample handing was performed under an argon atmosphere in a glove box. The x-ray diffraction measurements were performed using an automated powder diffractometer with Cu K_α radiation. Crystal structures were refined using GSAS.[8]

The ac susceptibility (0.5 mT at 137 Hz) and magnetization (up to 7 T) were measured using a commercial Quantum Design extraction magnetometer. Mössbauer spectra were collected using a constant acceleration spectrometer with a 74 MBq ^{119}Sn $BaSnO_3$ source. The system was calibrated using α-Fe and a ^{57}Co source mounted on the back of the drive. The temperature was varied from room temperature to 9 K using a vibration-isolated closed-cycle refrigerator. Spectra were fitted with Lorentzian sextets using a conventional least-squares minimization routine.

III. RESULTS AND DISCUSSION

The structural phase diagram of $Nd_5Si_xSn_{4-x}$ (Fig. 1) is simpler than that of $Nd_5Si_xGe_{4-x}$,[4] in that exhibits it only an orthorhombic form for $x \leqslant 3.5$ and steady contraction of the unit cell with an increase in x. The crystal structure switches abruptly from orthorhombic to tetragonal at the Si-rich end of the phase diagram ($x > 3.5$). The lattice parameters and unit cell volume decrease linearly with an increase in silicon content. The decrease in volume is in excellent agreement

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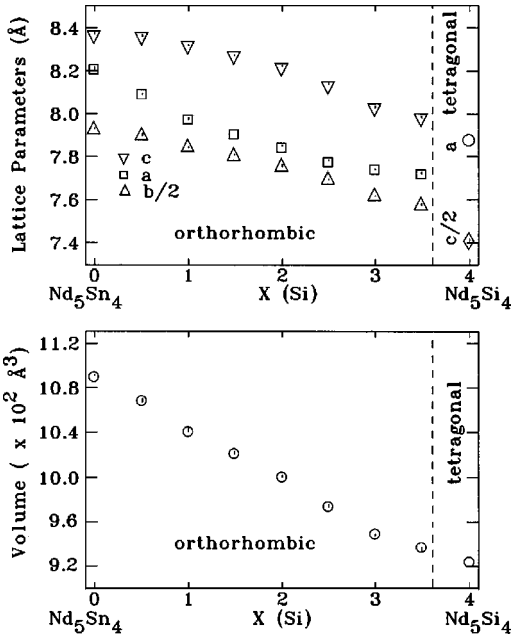

FIG. 1. Top: Composition dependence of the lattice parameters and crystal symmetry for $Nd_5Si_xSn_{4-x}$. Bottom: Unit cell volume vs *x*. The observed linear decrease is consistent with the difference in atomic size between Sn and Si.

with the difference in atomic size between Sn and Si. The fractional decrease in the unit cell from $x=0$ to 4 is 19%. Using atomic radii of 1.82 Å for Nd, 1.62 Å for Sn, and 1.32 Å for Si, the calculated fractional change in volume is 20%.

The temperature dependence of the ac susceptibility for these materials exhibits the same peaked behavior reported for $Nd_5Si_xGe_{4-x}$,[5] and it is therefore unlikely that they exhibit simple ferromagnetic ordering. The ordering temperature increases steadily from ~33 K at $x=0$ to ~120 K by $x=3.5$ (Fig. 2), the only exception being the abrupt drop by a factor of 2 at $x=4$ for the tetragonal Nd_5Si_4 alloy. The second transition (at ~85 K) in the $x=0$ alloy was shown by ^{119}Sn Mössbauer spectroscopy (see below) to be associated with an impurity phase.

While magnetization curves for these materials at 5 K exhibit a significant ferromagnetic response, they are far short of saturation at 7 T, and exhibit a substantial high-field slope. The initial approach to saturation is complete by 0.5 T,

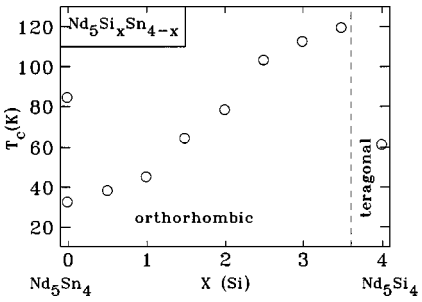

FIG. 2. Magnetic ordering temperatures for $Nd_5Si_xSn_{4-x}$ obtained from ac susceptibility. The 85 K event in Nd_5Sn_4 is due to an impurity phase. The vertical dashed line marks the position of the structural change identified in Fig. 1.

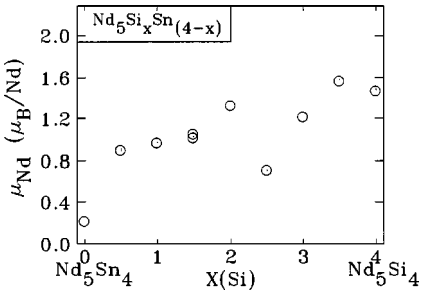

FIG. 3. Magnetization extrapolated linearly to zero field from above 0.5 T for $Nd_5Si_xSn_{4-x}$ at 5 K expressed as μ_B/Nd. The lower values at $x=0$ and 2.5 reflect the two-stage magnetization process observed at these compositions.

above this field the samples exhibited an almost linear increase which was least-squares fitted and extrapolated to zero field to obtain an estimate of the average ferromagnetic component of the ordered Nd moment (Fig. 3). The Nd moment derived increases by about a factor of 2 with an increase in Si content, but remains well below the $3.27\mu_B$ expected for the free-ion Nd moment. We interpret these reduced moments as reflecting a complex ordering of the Nd moments in a manner that exhibits both ferromagnetic and antiferromagentic modes, as has been reported in Nd_5Si_4 and Nd_5Ge_4.[5] In addition, both the $x=0$ and 2.5 samples exhibit breaks in their magnetization curves, with their magnetization jumping by almost a factor of 2 with an increase in field. The values reported in Fig. 3 are derived from the lower field region and therefore appear lower. These greatly reduced ferromagnetic components at $x=0$ and 2.5 suggest that the magnetic structures of these two alloys are quite different from those of the other orthorhombic alloys in this system. Since our ^{119}Sn Mössbauer data (see below) show no evidence of the first-order magnetic and structural transitions previously seen in both $Gd_5Si_xGe_{4-x}$ (Refs. 1–3) and Gd_5Sn_4,[7] we attribute the breaks in magnetization to some form of spin-flop event.

^{119}Mössbauer spectra of $Nd_5Si_xSn_{4-x}$ measured at 9 K all show a significant transferred field at the Sn sites, reflecting ordering of the Nd moments. At 10–16 T (Fig. 4), the transferred hyperfine fields in $Nd_5Si_xSn_{4-x}$ are far smaller than the 30–37 T observed in $Gd_5Si_xSn_{4-x}$.[6,7] The difference is almost a factor of 3, too large to be attributed simply to the smaller Nd moment and must also reflect a partially antiferromagnetic ordering of those Nd moments, consistent with the magnetization data in Fig. 3. While the fields are

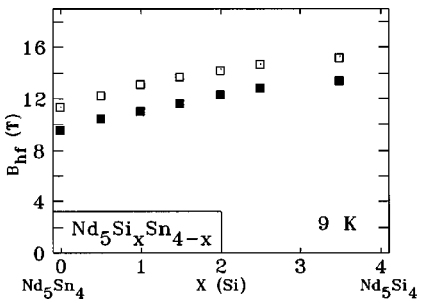

FIG. 4. Composition dependence of the ^{119}Sn hyperfine fields at 9 K for $Nd_5Si_xSn_{4-x}$.

much smaller than in $Gd_5Si_xSn_{4-x}$, the area ratio of the two components in the Nd alloys is comparable to that seen in the Gd series, with the larger-field component having about half the area of the smaller-field one. The composition dependence presented in Fig. 4 shows a gradual increase with x, thus mirroring the trends in both the ordering temperature and magnetization reported above. By contrast, the hyperfine fields at the Sn sites in the ferromagnetic $Gd_5Si_xSn_{4-x}$ alloy system were found to be essentially composition independent.[6] Some of the increase in hyperfine fields for $Nd_5Si_xSn_{4-x}$ will be due the increase in ordering temperature of the alloys (Fig. 2), however changes in the balance between antiferromagnetic and ferromagnetic contributions to the Nd ordering, seen in the increased magnetization, must also be a factor. It is interesting to note that there is no change in the transferred hyperfined fields at $x=0$ and 2.5 where the lower ferromagnetic contributions were noted in the magnetization data. Examination of the temperature dependences of the hyperfine fields in all of these alloys shows only a smooth progression with increasing temperature, with no evidence of a first-order structural change in any alloy. Finally, the severely broadened magnetic pattern that dominates the spectra of $Gd_5Si_xSn_{4-x}$ for $0.4 \leqslant x \leqslant 2.4$ appears to be entirely absent from the spectra of $Nd_5Si_xSn_{4-x}$. Since this feature was associated with the magnetocaloric transition in Gd_5Sn_4,[7] it is likely that no giant magnetocaloric effect will be observed in the $Nd_5Si_xSn_{4-x}$ system.

IV. CONCLUSIONS

The structural and magnetic properties of $Nd_5Si_xSn_{4-x}$ and $Nd_5Si_xGe_{4-x}$ are quite similar although the $Nd_5Si_xSn_{4-x}$ lacks the monoclinic form observed in $Nd_5Si_xGe_{4-x}$. Increasing the Si content leads to monotonic increases in both the magnetization and ordering temperature. The $Nd_5Si_xGe_{4-x}$ is known to exhibit mixed antiferromagnetic and ferromagnetic order, and the strong similarities between it and the Sn-doped system make it likely that such ordering will also be observed here. While spin-flop events were observed at 5 K at $x=0$ and 2.5, we found no evidence of the combined first-order structural and magnetic transition that leads to the giant magnetocaloric effect in $Gd_5Si_xGe_{4-x}$ and Gd_5Sn_4. A complete neutron scattering study is planned for the near future.

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