Magnetostructural transition in $Nd_5Si_{2.335}Ge_{1.665}$

H. B. Wang,[1] Z. Altounian,[1,a)] D. H. Ryan,[1,b)] J. M. Cadogan,[2] I. P. Swainson,[3] and L. M. D. Cranswick[3]
[1]*Centre for the Physics of Materials, Department of Physics, Rutherford Physics Building, McGill University, 3600 University St., Montreal, Quebec H3A 2T8, Canada*
[2]*Department of Physics and Astronomy, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*
[3]*Canadian Neutron Beam Centre, National Research Council, Chalk River Laboratories, Ontario K0J 1J0, Canada*

(Presented on 7 November 2007; received 4 October 2007; accepted 5 December 2007; published online 28 February 2008)

Neutron diffraction and χ_{ac} data show that the first order magnetostructural transition in the $Nd_5Si_xGe_{4-x}$ system takes place over a very narrow composition range ($2.25<x<2.5$) and does not appear to be controlled by the presence of light element impurities in the Nd metal. The structural change in $Nd_5Si_{2.335}Ge_{1.665}$ is from the $Gd_5Si_2Ge_2$-type monoclinic $P112_1/a$ structure (M) (room temperature) to the Gd_5Si_4-type orthorhombic $Pnma$ [O(I)] structure (low temperature). © *2008 American Institute of Physics*. [DOI: 10.1063/1.2838996]

I. INTRODUCTION

The discovery of the giant magnetocaloric effect (GMCE) in $Gd_5Si_xGe_{4-x}$ compounds[1] has stimulated a wider interest in magnetocaloric materials. The closely related structures observed in the $Gd_5Si_xGe_{4-x}$ system are based on the stacking of identical two-dimensional subnanometer thick slabs, with only the different arrangements of the $T1-T1$ ($T1$=Si or Ge) bonds between the slabs determining the final crystallographic structure.[2] Studies have revealed that the GMCE in $Gd_5Si_xGe_{4-x}$ is a result of a first order magnetostructural transition facilitated by the small crystallographic differences between the structures. The high neutron absorption cross section of natural gadolinium makes it effectively impossible to characterize magnetic structures for $Gd_5Si_xGe_{4-x}$ compounds; therefore, GMCE studies have expanded to other $R_5Si_xGe_{4-x}$ pseudobinary systems (R is a rare earth element),[3,4] where neutron diffraction can be used.

Recently, Magen *et al.*[5] studied $Nd_5Si_{2.4}Ge_{1.6}$ and found evidence of a coupled magnetic and structural transformation. They suggested that the failure to observe magnetostructural transformations in earlier studies of $Nd_5Si_xGe_{4-x}$ (Refs. 3, 6, and 7) may be due to the presence of the light element impurities (H, C, N, and O) in the constituent Nd metal.[5] In this paper, we present a study of the structural and magnetic properties of $Nd_5Si_xGe_{4-x}$ compounds prepared using commercial grade Nd metal and focus on $Nd_5Si_{2.335}Ge_{1.665}$ where we observe the magnetostructural transformation. We argue that the apparent contradiction between the earlier results[3,6,7] and those of Magen *et al.*[5] is not due to impurities but rather reflects the extremely narrow composition range over which the magnetostructural instability exists.

II. EXPERIMENTAL METHODS

For the initial survey of magnetic and structural properties, we prepared samples of $Nd_5Si_xGe_{4-x}$ (with x=0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4) in a triarc furnace with a base pressure of 6×10^{-7} mbar. Stoichiometric amounts of 99.9 wt % Nd, 99.9999 wt % Si, and 99.999 wt % Ge (all elements purchased from Alfa Aesar) were melted under pure argon. To ensure homogeneity, the samples were remelted several times. The ac susceptibility (χ_{ac}, using an ac field of 0.5 mT at 337 Hz) was measured using a commercial Quantum Design physical property measurement system extraction magnetometer. Neutron powder diffraction experiments were carried out at the Canadian Neutron Beam Centre using the DUALSPEC C2 800-wire powder diffractometer at the NRU reactor, Chalk River Laboratories. The neutron diffraction data at 280 K were collected between 3° and 113° in two banks with a wavelength of 1.3300(1) Å to permit accurate determination of the atomic thermal parameters during the structural refinement. Low temperature data were collected between 3° and 83° in one bank with a wavelength of 2.371 54(12) Å. All diffraction patterns were refined by the Rietveld method using the GSAS/EXPGUI suite of programs.[8]

III. RESULTS AND DISCUSSION

The magnetic ordering temperature of $Nd_5Si_xGe_{4-x}$ increases steadily with increasing silicon content (Fig. 1), showing a weak dependence on Si concentration for $x<2.5$. For $2.5<x<3.5$, the ordering temperature is almost double, which is seen at lower Si concentrations, but jumps back to the original low-Si values for $x>3.5$. Structural analysis confirmed that the high ordering temperatures were associated with $Nd_5Si_xGe_{4-x}$ adopting the orthorhombic Gd_5Si_4-type O(I) structure. The drop in ordering temperature at x=3.5 marks a change in room temperature structure from O(I) to the tetragonal Zr_5Si_4-type (T) form, a combination that, as yet, has not been associated with GMCE behavior because of the significant differences between the O(I) and T

a)Author to whom corresponding should be addressed. Tel.: 1 514 398 6535. FAX: 1 514 398 6525. Electronic mail: zaven@physics.mcgill.ca.
b)Electronic mail: dhryan@physics.mcgill.ca.

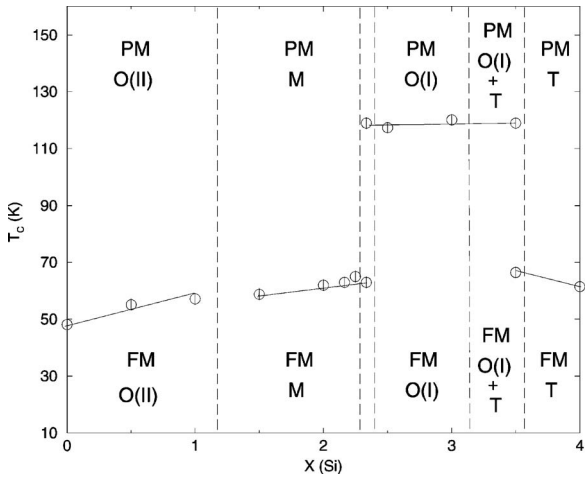

FIG. 1. Magnetic and structural phase diagram for $Nd_5Si_xGe_{4-x}$. Magnetic transition temperatures were obtained from χ_{ac} data, while structural data came from refinement of room temperature neutron powder diffraction patterns. Note the abrupt change in T_C on passing from the monoclinic (M) region to the O(I) form at $x \sim 2.3$.

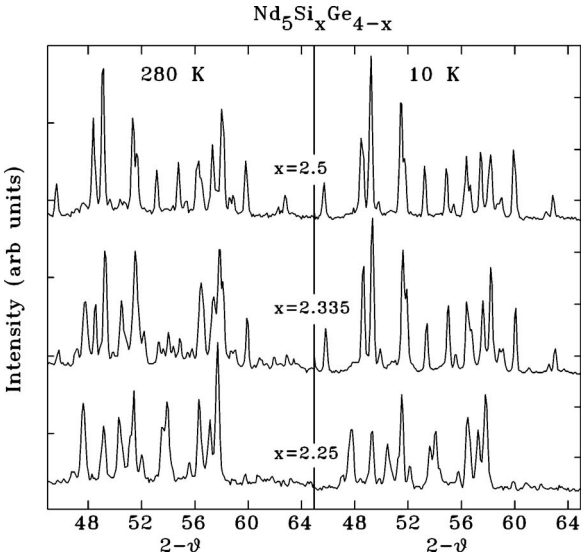

FIG. 2. Neutron diffraction patterns measured with $\lambda = 2.37154(12)$ Å for $Nd_5Si_xGe_{4-x}$ at 280 K (left) and 10 K (right), showing that for $x=2.5$, the compound remains in the O(I) form on cooling and the $x=2.25$ adopts the M form across the temperature range studied. By contrast, the $x=2.335$ compound changes from a $M+O$(I) mixture at 280 K (consistent with the χ_{ac} data in Fig. 3) to primarily O(I) at 10 K.

structures. However, the dramatic doubling of the magnetic ordering temperature [from 62(2) K at $x=2.0$ to 117(2) K at $x=2.5$] marks a change in room temperature structure from the monoclinic $Gd_5Si_2Ge_2$-type (M) form to the O(I) structure, and this combination of ordering temperature step and $M \rightarrow O$(I) structural change is characteristic of GMCE systems. The magnetic behavior of $Nd_5Si_xGe_{4-x}$ compounds suggested that a first order magnetostructural transformation was unlikely to take place in the O(II) or M phase regions as seen in $Gd_5Si_xGe_{4-x}$ and $Tb_5Si_xGe_{4-x}$ (Refs. 4 and 9) but could likely occur in the M:O(I) boundary region ($2 < x < 2.5$). Therefore, a finer search was undertaken with three new samples ($x=2.165$, 2.25, and 2.335) prepared between $x=2.0$ and 2.5. Samples with $x=2.165$ and 2.25 exhibited low [63(2) and 65(2) K, respectively] transition temperatures and adopted the monoclinic structure (Fig. 1); thus, the possible range over which a first order magnetostructural transformation could occur was found to be extremely limited ($2.25 < x < 2.5$). As we will show here, *only* the $Nd_5Si_{2.335}Ge_{1.665}$ sample was found to undergo a first order magnetostructural transition.

Neutron diffraction patterns for $x=2.25$, 2.335, and 2.5 are shown in Fig. 2, where we focus on the region of $45° < 2\vartheta < 65°$ highlighting several characteristic reflections. Prominent peaks at $2\vartheta = 46°$, 60°, and 63° serve as visual markers for the O(I) form confirming that the $x=2.5$ compound adopts the O(I) structure. Similarly, the peak at $2\vartheta = 47.5°$ is diagnostic for the M form and shows that the $x=2.25$ compound is monoclinic. Remarkably, the pattern for $x=2.335$ at 280 K shows markers from both forms, and χ_{ac} data for this compound (Fig. 3) show three magnetic transitions at 63(2), 93(2), and 119(2) K, corresponding to the Néel temperatures of the M phase, the hexagonal 5:3 compound (present as a minor impurity phase), and the O(I) phase, respectively.[10,11] Thus $Nd_5Si_{2.335}Ge_{1.665}$ occurs in both structural forms in the as-cast alloy at 280 K.

Our first indication of a magnetostructural transition in $Nd_5Si_{2.335}Ge_{1.665}$ came from χ_{ac} data, where we found that the strong signal from the M form at 63(2) K, clearly observed on cooling, was absent from the heating curve (inset of Fig. 4). The strength of the χ_{ac} peak at 63(2) K was used to monitor the regrowth of the M form after the sample had been converted to the O(I) form by cooling to 10 K. The sample was raised to progressively higher annealing temperatures, held for 10 min, and then cooled while recording χ_{ac} data. The relative height of the 63(2) K peak (normalized to that observed on first cooling from 290 K) is shown in Fig. 4. It is clear that the $O(I) \rightarrow M$ conversion occurs over a broad (~30 K wide) temperature range. It is also evident that there is substantial hysteresis associated with the O(I) $\rightarrow M$ conversion: the χ_{ac} were taken on recooling which requires us to cool *below* 60 K to observe the T_N of the M form, so although the formation of the M form has barely started at 70 K and is not complete until 100 K, back conversion to the O(I) form does not appear to start until below 60 K.

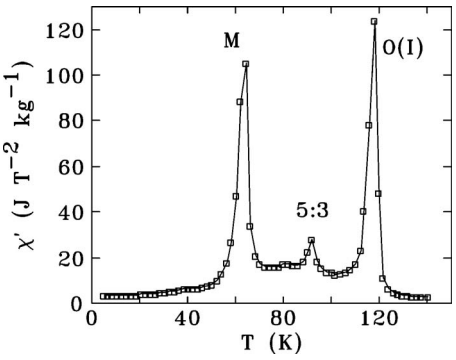

FIG. 3. ac susceptibility (χ_{ac}) data taken on cooling for $Nd_5Si_{2.335}Ge_{1.665}$ measured at 337 Hz using a 0.5 mT ac field. The ordering of the M and O(I) forms at 63(2) and 119(2) K, respectively, shows that both are present. The peak at 93(2) K is due to a minor $Nd_5(Si,Ge)_3$ impurity.

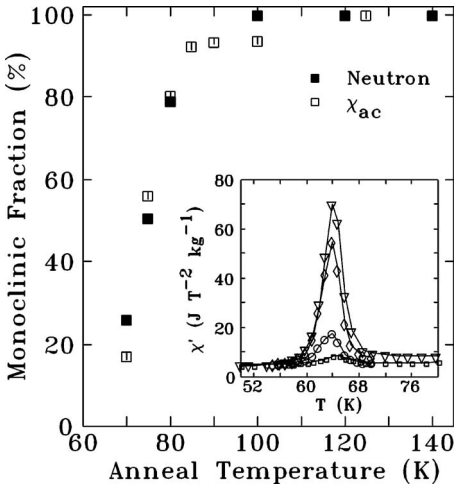

FIG. 4. Annealing temperature dependence of the monoclinic fraction present in the sample following cooling to 10 K. Data are taken from neutron diffraction (■, measured at the annealing temperature) and χ_{ac} (□, measured on cooling from the annealing temperature). Inset shows $\chi_{ac}(T)$ at around the 63(2) K magnetic ordering temperature of the monoclinic phase. On initial cooling (△), there is a strong signal from the M phase, but on reheating from 10 K (□), the signal is essentially gone. Data taken on cooling following annealing at 75 (○) and 85 K (◇) show the progressive regrowth of the monoclinic form.

Inspection of the neutron diffraction patterns at 10 K (right panel of Fig. 2) also shows evidence for the temperature induced $M \rightarrow O(\mathrm{I})$ conversion in $Nd_5Si_{2.335}Ge_{1.665}$. It is clear that the patterns for $x=2.5$ and 2.25 do not change significantly on cooling, while the 10 K pattern for $x=2.335$ shows a clear growth in all of the $O(\mathrm{I})$ marker peaks and loss of the peaks associated with the monoclinic form.

Refinement of the 280 K neutron pattern for $Nd_5Si_{2.335}Ge_{1.665}$ confirms that the sample is a two-phase mixture, with 87(1)% crystallizing in the M structure and 9(1)% in the $O(\mathrm{I})$ structure. A minor 4(1)% $Nd_5(Si,Ge)_3$ impurity phase was also detected. Fitted lattice parameters for the M phase are $a=7.7683(16)$ Å, $b=15.121(3)$ Å, and $c=7.9337(17)$ Å, with $\gamma=93.730(9)°$. By contrast, analysis at 10 K reveals that $Nd_5Si_{2.335}Ge_{1.665}$ now adopts the $O(\mathrm{I})$ structure, with the $Pnm'a'$ magnetic symmetry. The lattice parameters at 10 K are $a=7.6998(8)$ Å, $b=15.0816(16)$ Å, and $c=7.9388(8)$ Å. The average Nd magnetic moment was found to be $2.7(2)\mu_B$, somewhat smaller than the $3.06(5)\mu_B$ reported for $Nd_5Si_{2.4}Ge_{1.6}$.[5] Fitting a sequence of neutron diffraction patterns obtained at successively higher annealing temperatures allowed us to follow the regrowth of the monoclinic form directly. The results of this analysis are shown as solid symbols in Fig. 4 and are in complete agreement with the results taken from χ_{ac} shown as open symbols. There is clearly a significant coexistence region associated with the magnetostructural transformation in $Nd_5Si_{2.335}Ge_{1.665}$, as both techniques show that the evolution from $O(\mathrm{I})$ to M on heating occurs over a 30 K temperature range from 70 to 100 K. This is consistent with the first order nature of such transitions.

IV. CONCLUSIONS

Contrary to earlier reports that the magnetostructural transformation in $Nd_5Si_xGe_{4-x}$ is affected by the presence of light element impurities in the neodymium used to prepare the compounds,[5] we have found that the composition range over which the transformation is possible is remarkably narrow, spanning at most 6% of the total range from Nd_5Ge_4 to Nd_5Si_4. While it is still possible that low levels of impurities may play a role, it is more likely that the difficulties reported in observing the magnetostructural transition in $Nd_5Si_xGe_{4-x}$ reflect the challenges associated with achieving the precise composition in a very narrow target range: $2.25<x<2.5$.

[1] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[2] W. Choe, V. K. Pecharsky, A. O. Pecharsky, K. A. Gschneidner, Jr., V. G. Young, Jr., and G. J. Miller, Phys. Rev. Lett. **84**, 4617 (2000).
[3] K. A. Gschneidner, Jr., V. K. Pecharsky, A. O. Pecharsky, V. V. Ivtchenko, and E. M. Levin, J. Alloys Compd. **303–304**, 214 (2003); H. F. Yang, G. H. Rao, G. Y. Liu, Z. W. Ouyang, W. F. Liu, X. M. Feng, W. G. Chu, and J. K. Liang, J. Alloys Compd. **346**, 190 (2002).
[4] C. Ritter, L. Morellon, P. A. Algarabel, C. Magen, and M. R. Ibarra, Phys. Rev. B **65**, 094405 (2002).
[5] C. Magen, L. Morellon, P. A. Algarabel, M. R. Ibarra, C. Ritter, A. O. Pecharsky, K. A. Gschneidner, Jr., and V. K. Pecharsky, Phys. Rev. B **70**, 224429 (2004).
[6] H. F. Yang, G. H. Rao, G. Y. Liu, Z. W. Ouyang, W. F. Liu, X. M. Feng, W. G. Chu, and J. K. Liang, Physica B **325**, 293 (2003); C. Magen, C. Ritter, L. Morellon, P. A. Algarabel, and M. R. Ibarra, J. Phys.: Condens. Matter **16**, 7427 (2004).
[7] J. M. Cadogan, D. H. Ryan, Z. Altounian, H. B. Wang, and I. P. Swainson, J. Phys.: Condens. Matter **14**, 7191 (2002).
[8] A. C. Larson and R. B. Von Dreele, "General Structure Analysis System, (GSAS)," Los Alamos National Laboratory Report No. LAUR 86-748, 2000; B. H. Toby, J. Appl. Crystallogr. **34**, 210 (2001).
[9] V. K. Pecharsky and K. A. Gschneidner, Jr., J. Alloys Compd. **260**, 98 (1997).
[10] A. O. Pecharsky, K. A. Gschneidner, Jr., V. K. Pecharsky, and C. E. Schindler, J. Alloys Compd. **338**, 126 (2002).
[11] P. Schobinger–Papamantellos, and K. H. J. Buschow, J. Magn. Magn. Mater. **49**, 349 (1985); P. Boulet, F. Weitzer, K. Hiebl, and H. Noël, J. Alloys Compd. **315**, 75 (2001).