The temperature induced structural transformation in $Gd_5Si_xSn_{4-x}$ (x = 0 and 0.4)

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Abstract
Low temperature synchrotron x-ray diffraction data confirm that a temperature induced structural transformation accompanies the previously reported first-order magnetic transition in $Gd_5Si_xSn_{4-x}$ (x = 0 and 0.4). The structural change is from the orthorhombic *Pnma* Gd_5Ge_4-type (room temperature) to the orthorhombic *Pnma* Gd_5Si_4-type (low temperature). The transformation in Gd_5Sn_4 is not complete by 20 K, with about 13% of the high temperature Gd_5Ge_4-type structure remaining. These results are in excellent agreement with previous Mössbauer and magnetic measurements.

1. Introduction

Interest in magnetocaloric materials was rekindled by the discovery of the near room temperature giant magnetocaloric (GMC) effect in $Gd_5Si_xGe_{4-x}$ ($0.96 \leqslant x \leqslant 2.0$) [1]. The GMC effect is the result of a magnetostructural transition from monoclinic-paramagnetic to orthorhombic-ferromagnetic upon cooling [2, 3]. Recently, a similar effect has been reported in Ge-rich $Gd_5Si_xGe_{4-x}$ compounds ($0 \leqslant x \leqslant 0.4$) [4–7]. Here, the magnetostructural transformation is from orthorhombic (Gd_5Ge_4-type)-antiferromagnetic to orthorhombic (Gd_5Si_4-type)-ferromagnetic. In both cases, the magnetostructural transition can be induced by temperature, magnetic field or pressure. The high neutron absorption cross section of natural gadolinium limits the direct determination of the 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) [8–10], 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

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inequivalent Sn atom. This has led to the observation of a first-order magnetic transition (from ferromagnetic to nonmagnetic) at 82 K in Gd_5Sn_4 and at 106 K in $Gd_5Si_{0.4}Sn_{3.6}$ [11]. We suggested that the magnetic transition is likely to be coupled with a structural transition in these compounds. Subsequent bulk magnetization and ^{119}Sn Mössbauer spectroscopy studies on Gd_5Sn_4 with an applied magnetic field confirmed that Gd_5Sn_4 exhibits a giant magnetocaloric effect [12] associated with the first-order magnetic change at 82 K, and that this transition can be reversed by an external magnetic field. Moreover, our ^{119}Sn Mössbauer study on Gd_5Sn_4 revealed that [11]:

(1) a weak broad singlet is still present at 12 K, accounting for about 4% of the total area;
(2) upon warming, the sharp magnetic components persist to 80 K, with the nonmagnetic singlet accounting for only about 37% of the total area;
(3) on passing through 80 K, the sharp magnetic components vanish abruptly.

These results demonstrated that temperature drives a first-order magnetic transformation in Gd_5Sn_4, and that this transformation is not complete at 80 K upon warming. We also inferred that the magnetic transition is likely to be accompanied with a structural change between two closely related orthorhombic forms as seen in $Gd_5Si_{0.4}Ge_{3.6}$ [5].

Recently, Yang *et al* [13] studied Gd_5Sn_4 by temperature dependent Cu Kα x-ray diffraction and did not observe the predicted structural transition on cooling to 80 K. This might appear to conflict with our expectations based on ^{119}Sn Mössbauer data [11, 12]; however, the structural transition is first-order and some hysteresis is inevitable. Reported transition widths in related systems range from ∼5 K in $Gd_5Si_{0.4}Ge_{3.6}$ [14] to ∼12 K in $Gd_5Si_{1.5}Ge_{2.5}$ [15]. Given that we observed the transition to be at 82 K on heating, it is likely that cooling below 80 K is necessary to induce a measurable degree of transformation.

We have therefore performed synchrotron x-ray experiments down to a much lower temperature (20 K) to avoid temperature hysteresis and obtain accurate structural information. In particular, the changes in lattice parameters and the Sn–Sn interatomic distances, which characterize the difference of Gd_5Ge_4-type and Gd_5Si_4-type structures [16, 17], were calculated. In this paper, we present low temperature synchrotron x-ray results on $Gd_5Si_xSn_{4-x}$ with $x = 0$ and 0.4.

2. Experimental methods

Gd_5Sn_4 and $Gd_5Si_{0.4}Sn_{3.6}$ ingots were prepared in a tri-arc furnace with a base pressure of 6×10^{-7} mbar. Stoichiometric amounts of Gd (99.9 wt%, purchased from Alfa Aesar), Si (99.9999 wt%) and Sn (99.99 wt%) were melted under pure argon. To ensure homogeneity, the alloys were remelted several times. The compounds were air-sensitive, so all sample handling was performed in a glove box under a pure argon atmosphere. The powder samples were sealed in evacuated quartz tubes for transportation.

Synchrotron x-ray experiments were carried out at Beamline 2-1 of the Stanford Synchrotron Radiation Laboratory. The x-ray energy was chosen as 7200 eV (1.7217 Å), just below the Gd L-edge to increase the penetration depth (∼6 μm) while retaining a high angular resolution for the Bragg peaks. Low temperatures were achieved using a vibration-isolated closed-cycle He-refrigerator. The step size for all diffraction patterns was fixed at $0.02°$ of 2θ.

The synchrotron x-ray data at 295 K for Gd_5Sn_4 and $Gd_5Si_{0.4}Sn_{3.6}$ were collected between 28° and 110° to permit accurate determination of the atomic thermal parameters during the structural refinement. Low temperature data were collected between 28° and 90°. The diffraction patterns were refined by the Rietveld method using the GSAS program [18].

Table 1. Refined structural parameters for Gd_5Sn_4 at 295 and 20 K.

	295 K			20 K		
	$a = 8.0446(3)$	$b = 15.5404(5)$	$c = 8.2025(3)$	$a = 7.9263(2)$	$b = 15.4965(5)$	$c = 8.2278(2)$
Atom	x/a	y/b	z/c	x/a	y/b	z/c
Gd1(4c)	0.3112(8)	0.25	−0.0063(6)	0.3405(11)	0.25	0.0042(7)
Gd2(8d)	−0.0245(5)	0.1000(2)	0.1786(5)	0.0008(7)	0.0942(3)	0.1782(4)
Gd3(8d)	0.3556(5)	0.8782(3)	0.1577(5)	0.3326(6)	0.8761(3)	0.1780(5)
Sn1(4c)	0.1759(8)	0.25	0.3523(7)	0.2112(10)	0.25	0.3481(8)
Sn2(4c)	0.9507(9)	0.25	0.8817(7)	0.9630(12)	0.25	0.8993(8)
Sn3(8d)	0.2051(7)	0.9595(3)	0.4669(6)	0.1746(8)	0.9602(3)	0.4691(5)

Texture effects were observed in the powder patterns, and the spherical harmonic function (in the GSAS program) was used to correct for the effects of preferential orientation.

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 12 K to room temperature using a vibration-isolated closed-cycle refrigerator.

3. Results and discussion

The x-ray pattern of Gd_5Sn_4 at 295 K is shown with the fit and difference plot in figure 1(a). Analysis of the x-ray pattern indicates that Gd_5Sn_4 adopts the orthorhombic *Pnma* Gd_5Ge_4-type structure at 295 K, with $a = 8.0446(3)$ Å, $b = 15.5404(5)$ Å and $c = 8.2025(3)$ Å. The atomic positions are given in table 1. About 5 wt% of the impurity phase $Gd_{11}Sn_{10}$ was also present.

Figure 1(b) shows the synchrotron x-ray pattern of Gd_5Sn_4 at 20 K. Pattern refinement demonstrates that Gd_5Sn_4 adopts the orthorhombic *Pnma* Gd_5Si_4-type structure at 20 K, with $a = 7.9263(2)$ Å, $b = 15.4965(5)$ Å and $c = 8.2278(2)$ Å. The structural transformation is incomplete, and about 13% of the Gd_5Ge_4-type structure still remains at 20 K. Atomic positions at 20 K are listed in table 1.

Our previous ^{119}Sn Mössbauer spectroscopy study [12] suggests that about 6% (interpolated value) of the material would be present in the room temperature structure type at 20 K upon warming, in agreement with 13% obtained from the analysis of the synchrotron x-ray pattern at 20 K upon cooling. The difference between these values is likely due to thermal hysteresis associated with the first-order nature of the structural transition. The synchrotron x-ray diffraction at 20 K confirms that the magnetic transition in Gd_5Sn_4 is indeed associated with a structural change between two closely related orthorhombic structures.

Synchrotron x-ray data for $Gd_5Si_{0.4}Sn_{3.6}$ were collected at temperatures of 295, 106, 95 and 15 K. To highlight the subtle differences in the diffraction patterns at different temperatures, the x-ray patterns are shown in the 2θ range of 32° and 42° in figure 2. The crystal structure of the $Gd_5Si_{0.4}Sn_{3.6}$ sample has the orthorhombic *Pnma* Gd_5Ge_4-type structure at 295 K, with Gd_5Sn_3 and $Gd_{11}Sn_{10}$ as impurity phases. Refinement of the patterns at different temperatures reveals that the material at both room temperature and 106 K adopts the Gd_5Ge_4-type structure, while at 95 and 15 K the structure is of the Gd_5Si_4-type.

The two orthorhombic structures are closely related, and as a consequence share many Bragg peaks. To distinguish the two structures, we have highlighted, in figure 2, those peaks that are unique to each structure. The downward facing arrows indicate the distinct Bragg peaks
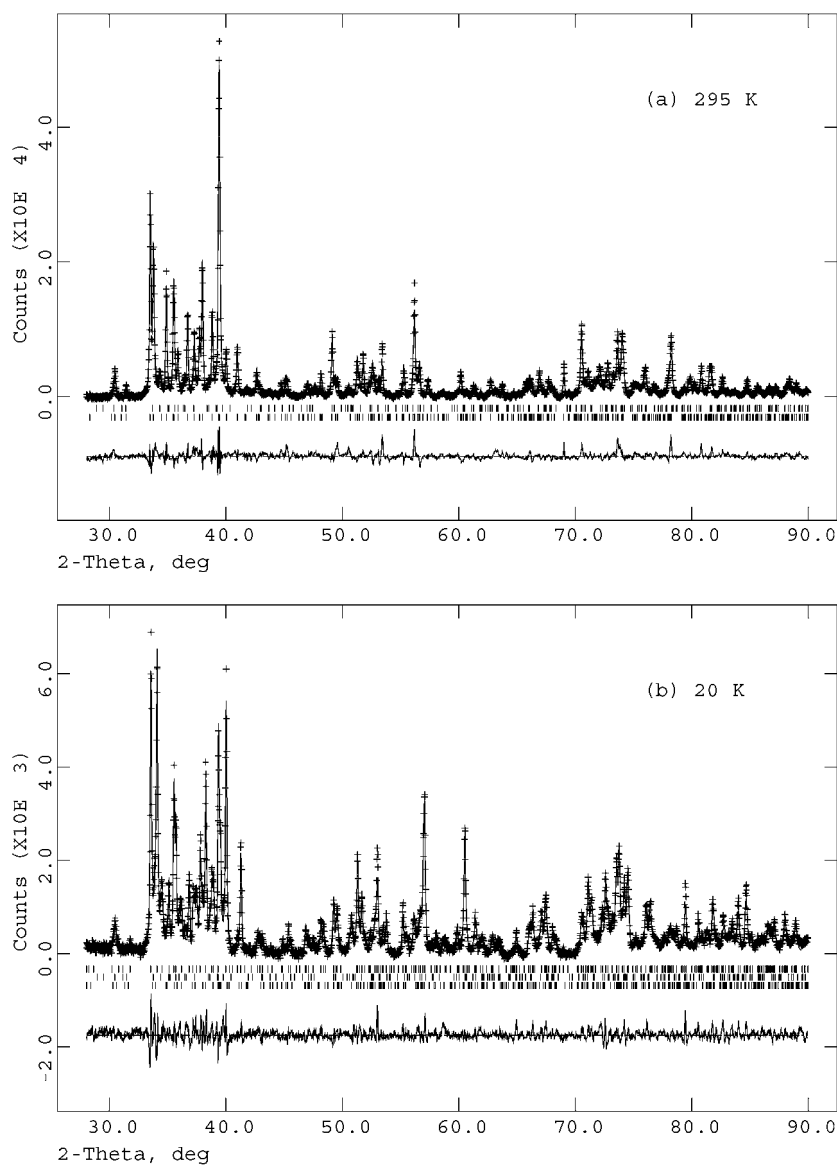
Figure 1. Synchrotron x-ray diffraction patterns of Gd_5Sn_4 at 295 K (a) and 20 K (b). The Bragg markers (from top to bottom) are $Gd_{11}Sn_{10}$ and Gd_5Sn_4 in the 295 K pattern, and Gd_5Sn_4 (Gd_5Si_4-type), $Gd_{11}Sn_{10}$ and Gd_5Sn_4 (Gd_5Ge_4-type) in the 20 K pattern.

corresponding to the Gd_5Ge_4-type (high-T), and the upward facing arrows indicate those from the Gd_5Si_4-type (low-T) structures. The change in structure is clearly observed upon cooling. Figure 3(a) shows ^{119}Sn Mössbauer spectra of $Gd_5Si_{0.4}Sn_{3.6}$ at several temperatures upon warming. The central component becomes more prominent, at the expense of the magnetic components, as the structure changes on heating. Similar changes were seen in Gd_5Sn_4 [11]. As figure 3(b) shows, the magnetic components disappear between 105 and 110 K, confirming the magnetic transition seen at ~106 K in AC-susceptibility data [11]. On passing through the
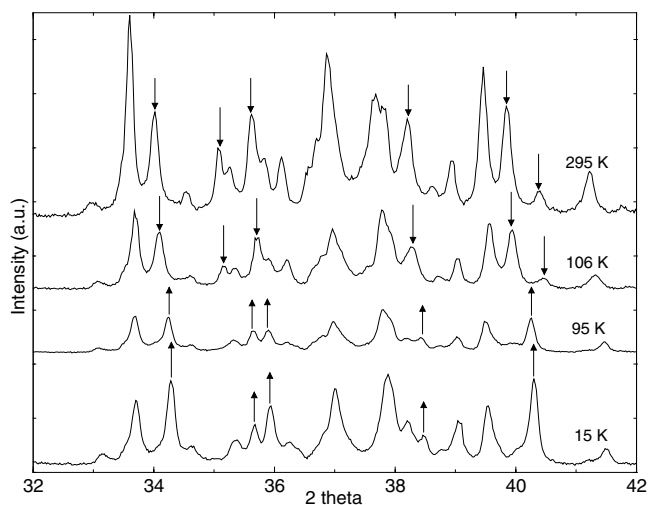
Figure 2. Synchrotron x-ray diffraction patterns of $Gd_5Si_{0.4}Sn_{3.6}$ at different temperatures. The downward facing arrows indicate the distinct Bragg peaks corresponding to the high-T Gd_5Ge_4-type structure, and the upward facing arrows indicate those to the low-T Gd_5Si_4-type structure.
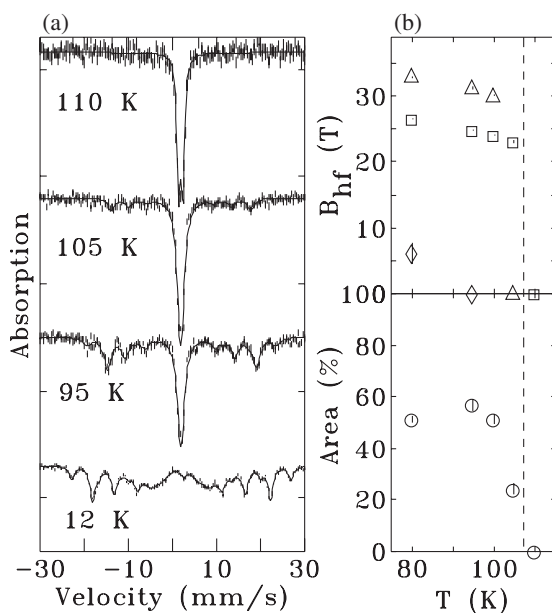

Figure 3. (a) ^{119}Sn Mössbauer spectra of $Gd_5Si_{0.4}Sn_{3.6}$ at several temperatures. This sample shows a transition above 105 K as the magnetic components disappear. (b) The temperature dependence of the hyperfine fields for the sharp ($\triangle$ and $\square$) and Gaussian-broadened ($\diamond$) components (top). The sharp sextets are lost on passing through 105 K. The area of the magnetic contributions to the ^{119}Sn Mössbauer spectra of $Gd_5Si_{0.4}Sn_{3.6}$ (bottom).

magnetic ordering temperature (~106 K), $Gd_5Si_{0.4}Sn_{3.6}$ undergoes a structural transformation. Therefore, the magnetostructural transition seen in Gd_5Sn_4 also occurs in $Gd_5Si_{0.4}Sn_{3.6}$.

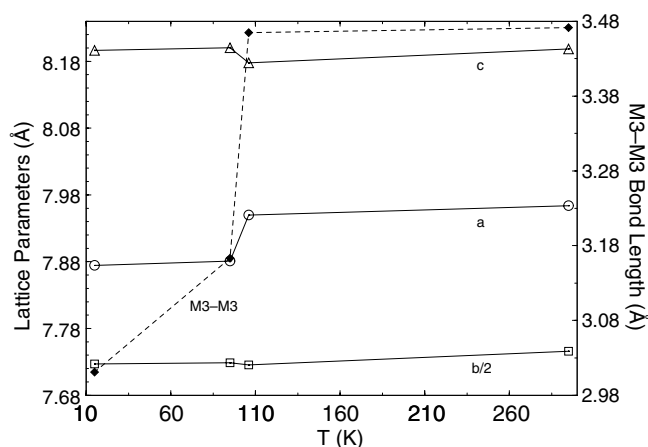**Figure 4.** The temperature dependence of the lattice parameters and the length of the M3–M3 (8d site) bonds in $Gd_5Si_{0.4}Sn_{3.6}$. The data were obtained from the refinement of synchrotron x-ray diffraction patterns at different temperatures.

Figure 4 shows the temperature dependence of the lattice parameters for $Gd_5Si_{0.4}Sn_{3.6}$. On passing through the magnetic transition temperature, a large change along the *a* axis is observed. The relative change in the *a* parameter between 295 and 20 K for $Gd_5Si_{0.4}Sn_{3.6}$ is $\Delta a/a = -1.1\%$, while for Gd_5Sn_4 $\Delta a/a = -1.5\%$. The contractions in *a* exceed those of *b* and *c* by a factor of nearly 5 in both alloys, implying that the structural changes cause the atoms to shift primarily along the *a* axis upon cooling through the magnetic transition. Furthermore, the changes between the Gd_5Ge_4-type and Gd_5Si_4-type structures are dominated by a large change in the length of the M3–M3 bonds (M = Si, Ge, Sn or a mixture of Si and Sn on the 8d site) [16, 17], with the M3–M3 bonds being significantly longer in Gd_5Ge_4-type compounds than they are in Gd_5Si_4-type compounds. Figure 4 shows the temperature dependence of the M3–M3 bond length in $Gd_5Si_{0.4}Sn_{3.6}$. An abrupt reduction of 15% is clearly seen upon cooling through the magnetic transition. Refinement of the Gd_5Sn_4 patterns also shows that the largest change in interatomic distance occurs between Sn atoms on the M3 sites in the different layers. On passing through the magnetic transition temperature, the distance between the M3 sites changes from 3.57 Å (295 K) to 3.07 Å (20 K), a contraction of 16%. The M3–M3 bonds become stronger at 20 K as a result of this contraction. Similar behaviour has been reported in $Gd_5Si_{0.4}Ge_{3.6}$ [5] on heating through the magnetic transition temperature, and in Gd_5Ge_4 [6] when a magnetic field was applied. The changes of the M3–M3 bond lengths in Gd_5Sn_4 and $Gd_5Si_{0.4}Sn_{3.6}$ are not as large as those seen in $Gd_5Si_{0.4}Ge_{3.6}$ (34%) and Gd_5Ge_4 (28%). This is probably due to the large atomic size of Sn relative to that of Si and Ge. The refinement results do not show any significant changes in the Gd–Gd distances in either Gd_5Sn_4 or $Gd_5Si_{0.4}Sn_{3.6}$, implying that it is the changes of the interlayer M3–M3 bond lengths that affect the nature of the magnetic interactions between Gd atoms, resulting in the magnetic transition.

4. Conclusions

Synchrotron x-ray diffraction studies have confirmed that both Gd_5Sn_4 and $Gd_5Si_{0.4}Sn_{3.6}$ undergo a temperature induced structural change upon cooling, from the orthorhombic *Pnma* Gd_5Ge_4-type (high temperature) structure to the orthorhombic *Pnma* Gd_5Si_4-type (low temperature) one. This structural change is accompanied by a first-order magnetic transition

from nonmagnetic to ferromagnetic. The temperature induced structural transformation in Gd$_5$Sn$_4$ is incomplete on cooling to 20 K.

Acknowledgments

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