Magnetic structure of GdNiSn

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The magnetic structure of the TiNiSi-type GdNiSn compound has been studied by both ^{155}Gd Mössbauer spectrocopy and neutron powder diffraction. The results suggest a square-wave modulated magnetic structure characterized by the propagation vector k = [0.426, 0.351, 0] and Gd magnetic moments of 6.52(15)μ_B (at 3.6 K) oriented along the *c*-axis. The results are compared with those of the isotypic RNiSn compounds and with the possible magnetic structures of GdNiSn proposed from earlier ^{155}Gd Mössbauer work. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4793642]

I. INTRODUCTION

The ternary equiatomic RTX (R = rare earth element; T = transition metal; X = p-block element) intermetallic compounds crystallize in many different structure types, among which the orthorhombic TiNiSi-type (space group *Pnma* No. 62) is one of the most common. Almost all of the antiferromagnetic structures of the RNiSn compounds, which crystallize in the TiNiSi-type structure, have been studied by neutron diffraction. These compounds are characterized by sine-wave modulated (SWM) magnetic structures, which transform in some cases to square-wave modulated (SqWM) at very low temperature.[1–5] Due to the large absorption cross section of natural Gd, there have been no neutron diffraction measurements of the GdNiSn compound. Kmieć *et al*. made ^{155}Gd Mössbauer measurements and tentatively proposed that GdNiSn has a collinear magnetic structure with the Gd moments lying in the *ab*-plane, or a noncollinear structure with the Gd moments slightly tilted from the *bc*-plane.[6]

Combining neutron powder diffraction data using a large area flat plate sample holder[7] with our own ^{155}Gd Mössbauer measurements, we have made a complete characterization of the magnetic structure of GdNiSn.

II. EXPERIMENTAL METHODS

Polycrystalline GdNiSn was synthesized by high frequency induction melting high purity elements in a water-cooled copper crucible under a pure argon atmosphere. The sample was then annealed in a silica tube under purified argon for 15 days at 973 K. X-ray diffraction showed the sample to be free of impurities and confirmed that GdNiSn crystallizes in the orthorhombic TiNiSi-type structure with refined cell parameters a = 7.212(1)Å, b = 4.482(1)Å, and c = 7.683(1)Å. Thermal neutron diffraction experiments were carried out at a neutron wavelength of 1.3286(1)Å on the C2 multi-wire diffractometer (DUALSPEC) at the Canadian Neutron Beam Center, Chalk River, Ontario. A large area silicon flat-plate sample holder[7] was used to minimise the effects of absorption by the natural Gd in the sample. Analysis of x-ray and neutron patterns was performed by Rietveld profile refinement using the FULLPROF software.[8] No absorption correction was applied, however, the neutron data were truncated at $2\theta = 53.3°$ to minimize the impact of angle-dependent absorption effects.

The sample and 50 mCi $^{155}SmPd_3$ source were mounted vertically in a helium flow cryostat, and the drive was operated in sine mode. The drive system was calibrated using a laser interferometer with velocities cross-checked against both ^{57}Co**Rh**/α-Fe at room temperature and $GdFe_2$ at 5 K.[9] The spectra were fitted using nonlinear least-squares minimization routine with line positions and intensities derived from an exact solution to the full Hamiltonian.[10] The electric quadrupole coupling constant (ground state) obtained from the fits is referred to as eQV_{zz}.

III. RESULTS AND DISCUSSION

The refined neutron pattern of GdNiSn recorded in the paramagnetic state (T = 20 K) is shown in the top panel of Figure 1. It exhibits only nuclear scattering, and confirms the TiNiSi-type structure seen by powder x-ray diffraction. Extra peaks due to the sample mount were observed in the $2\theta = 33–35°$ and $2\theta = 37–41°$ ranges, and were excluded from the refinements. There are clear additional purely magnetic peaks in the 3.6 K pattern (Figure 1), allowing us to rule out a conical magnetic structure. Short duration patterns recorded from 20 K down to 3.6 K reveal a magnetic ordering temperature $T_N = 10.9(2)$ K, in fair agreement with previous reports.[11,12] The 3.6 K neutron pattern of GdNiSn can be refined using either a planar helimagnetic structure (middle panel of Figure 1) or a SWM magnetic structure (bottom panel of Figure 1). However, as any harmonic peaks (i.e., A(3 k) = A(k)/3) from a SqWM structure would be within the noise level of the 3.6 K pattern, square-wave and sine-wave modulated structures are indistinguishable by neutron diffraction.

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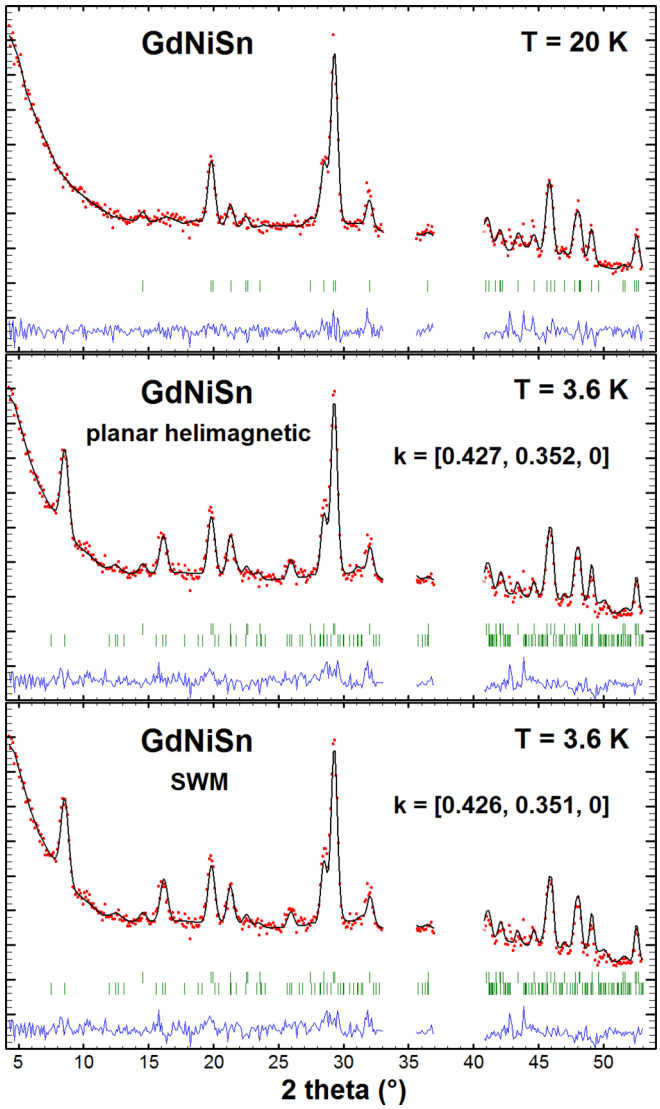

FIG. 1. Refinement of the neutron powder diffraction patterns of GdNiSn at 20 K and 3.6 K with $\lambda = 1.3286(1)$ Å. For the 3.6 K patterns, the top row of Bragg markers indicates the nuclear reflections and the lower set marks the magnetic reflections.

Both magnetic structures are characterized by a propagation vector k = [~0.43, ~0.35, 0], consistent with the general trend of the heavy rare-earth RNiSn compounds.[1–4] The best refinement obtained with the planar helimagnetic structure leads to the rotation of the magnetic moments in a plane slightly canted from the *ac*-plane and magnetic phases of 0, 0, 1/2, and 1/2 for the Gd atoms with positions (x; 1/4; z), (−x, 3/4, −z), (1/2 − x; 3/4; 1/2 + z), and (1/2 + x, 1/4, 1/2 − z), respectively. The best refinement obtained with the SWM magnetic structure leads to magnetic moments oriented along the *c*-axis, and magnetic phases of 0, 1/2, 5/6, and 2/3. For both magnetic structures, the refined moments are significantly smaller than the $7\mu_B$ expected for a Gd^{3+} ion (Table I). While the SWM refinement is slightly better, the relative closeness of the various refinement *R*-factors (Table I) means that it is not possible to determine unambiguously the correct magnetic structure from neutron diffraction measurements alone.

To identify the correct magnetic structure, ^{155}Gd Mössbauer spectra were taken in steps between 5 K and 15 K. The *4 c* site which the Gd atoms occupy has *.m.* symmetry (a mirror plane perpendicular to the *b*-axis). This forces one of the axes of the efg to be parallel to the *b*-axis. The remaining axes lie in the *ac*-plane. Another consequence of the symmetry of the site is that it is possible to have a non-zero asymmetry in the efg (η).

TABLE I. Results from the various refinements of the 3.6 K neutron diffraction pattern of GdNiSn.

a = 7.188(4) Å; b = 4.472(3) Å; c = 7.674(4) Å			
Helimagnetic		Sinusoidal/Square	
q_x	0.427(4)	q_x	0.426(4)
q_y	0.352(3)	q_y	0.351(3)
θ_c (°)	90	$A(k)_{Gd}$	8.30(19)
θ (°)	90	θ (°)	0
ϕ (°)	108(2)	ϕ (°)	0
Magnetic phases	0;0;0.5;0.5	Magnetic phases	0;0.5;0.83;0.67
μ_{Gd} (μ_B)	5.98(16)	μ_{Gd} (μ_B)	5.87(14)/6.52(15)
R(Bragg); R(F)	21.8; 17.2	R(Bragg); R(F)	20.1; 16.4
R(Magn)	24.2	R(Magn)	22.8
R(wp); R(exp)	3.31; 1.74	R(wp); R(exp)	3.27; 1.74
χ^2	3.65	χ^2	3.54

The 15 K pattern, shown in the top of Figure 2, is paramagnetic and was used to determine $eQV_{zz} = 1.84(1)$ mm/s. Since η and eQV_{zz} cannot be individually determined in a paramagnetic ^{155}Gd Mössbauer spectrum, $\eta = 0$ was assumed as a starting point to the fits, and worked quite well.

The two possible magnetic structures lead to very different Gd environments and so two models were developed to fit the ^{155}Gd Mössbauer spectra. The first, used to simulate the planar

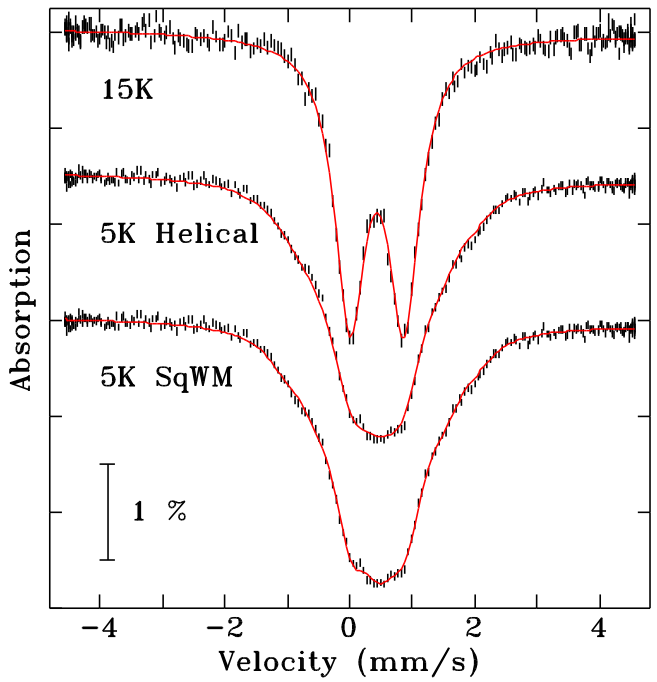

FIG. 2. ^{155}Gd Mössbauer refinements of GdNiSn at 15 K and 5 K. The 15 K spectrum is in the paramagnetic regime. The two 5 K fits are, from top to bottom, the planar helimagnetic (helical) model (60 site fit), and the SqWM model (single site fit).

helimagnetic structure, approximated the incommensurate propagation vector by the commensurate k = [2/5, 1/3, 0]. This leads to 60 magnetic sites (the magnetic unit cell is 5 and 3 times larger along the *a*- and *b*- axes, respectively, than the crystallographic unit cell). The isomer shift, hyperfine field (B_{hf}) and eQV_{zz} were constrained to the same value across the 60 sites, and the symmetry of the site was taken into account when setting the angles (θ) between the principal axis of the efg (V_{zz}) and the hyperfine field.

The second model, used to simulate the modulated structure, was much simpler. Simulations of a SWM field distribution led to centrally peaked spectra and the fitting program would compensate by lowering eQV_{zz} (relative to the paramagnetic spectrum), while maintaining the normal linewidth seen in ^{155}Gd (~0.33 mm/s). By contrast, a single-site fit was found to work well, with eQV_{zz} independent of temperature, suggesting *square*-wave rather than *sine*-wave modulation.

For each model, there are also two possible efg orientations to take into account: V_{zz} parallel to the *b*-axis, or in the *ac*-plane. Attempting to fit the two models with V_{zz} parallel to the *b*-axis yielded poor results, with very visible misfits. The two models were then tried with the V_{zz} axis in the *ac*-plane. For the planar helimagnetic structure, the fits were good ($\chi^2 = 1.15$), with an angle (α) of 60(20)° between V_{zz} and the *c*-axis. For the SqWM structure, the fits were better ($\chi^2 = 1.02$), with $\alpha = 52(1)^\circ$.

Even with more sites and more parameters to refine, the planar helimagnetic fit in Figure 2 is visibly inferior to the square-wave fit. The SqWM structure moment is $\mu_{Gd} = 6.52(15)\mu_B$ at 3.6 K, giving a moment of $6.86(16)\mu_B$ at T = 0 K, fully consistent with the expected value of $7\mu_B$. While the helimagnetic and SWM/SqWM magnetic structures could not be distinguished on the basis of neutron diffraction alone, the clear superiority of the SqWM fit to the 5 K Mössbauer spectrum, combined with the expected Gd moment derived from the SqWM fit to the neutron diffraction data allows us to formally assign the SqWM structure to GdNiSn.

This magnetic structure is inconsistent with previous Mössbauer work by Kmieć *et al.*,[6] who used $Gd_{0.1}Tb_{0.9}NiSn$ to derive $\eta = 0.74(11)$ and the orientation of V_{zz} (parallel to the *c*-axis, i.e., $\alpha = 0^\circ$). However, their fit to GdNiSn then gave $\alpha = 40(3)^\circ$, implying a change in the orientation of V_{zz}, which seems unlikely. Our visual evaluation of their spectrum for $Gd_{0.1}Tb_{0.9}NiSn$ suggests that a pattern with $\eta = 0$ and $\alpha \sim 50^\circ$ would fit their data and be more consistent with our results.

IV. CONCLUSION

By combining ^{155}Gd Mössbauer spectroscopy and neutron powder diffraction measurements, we have been able to show that the TiNiSi-type GdNiSn compound adopts an incommensurate SqWM antiferromagnetic structure with moments oriented along the *c*-axis. While the absence of the first odd integer harmonic diffraction peaks might suggest sine-wave modulation, these peaks are expected to be too weak to be observed and the shape of the ^{155}Gd Mössbauer spectrum at 5 K rules out sine-wave modulation. The magnetic structure is consistent with those previously reported with the heavy rare-earth TiNiSi-type RNiSn compounds.

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