

Magnetic ordering in GdAgSb₂

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Abstract

GdAgSb₂ has been studied using ¹⁵⁵Gd Mössbauer spectroscopy and neutron powder diffraction at a wavelength of 2.3672(1) Å. Commensurate antiferromagnetic order develops below $T_N = 13.8(4)$ K with the 6.2(3) μ_B Gd moments lying in the *ab*-plane of the tetragonal cell. The magnetic ordering is characterized by a $[\frac{1}{2} 0 0]$ propagation vector (i.e. the magnetic cell is doubled along one of the crystallographic basal plane axes) with the Gd moments oriented perpendicular to the doubled direction. These results are fully consistent with an earlier determination by x-ray resonant magnetic exchange scattering.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The RAgSb₂ compounds crystallize in the tetragonal ZrCuSi₂-type structure (space group $P4/nmm$ No. 129) with the rare earth atom occupying the 2c positions (point symmetry $4mm$) [1, 2]. The compounds have been prepared for R = Y, La–Tm, with the usual exceptions of Pm and Eu. The anisotropic thermodynamic and transport properties of this family were reported by Myers *et al* [3–5], and a subsequent neutron diffraction study by André *et al* showed that all of the compounds were collinear antiferromagnets (AFMs) below their Néel temperatures which were typically less than 13 K [6]. The exception was CeAgSb₂ which was found to be ferromagnetic with $T_c = 9.5$ K [3]. As is conventional in such neutron scattering studies, the gadolinium and samarium compounds were omitted as the large absorption cross-sections (particularly in the case of Gd) render neutron diffraction studies somewhat challenging. The availability of high quality single crystals of the RAgSb₂ compounds [3] made it possible to use x-ray resonant exchange scattering measurements to investigate the magnetic structure of GdAgSb₂ [7] and a planar AFM structure characterized by a $[\frac{1}{2} 0 0]$ propagation vector was deduced.

Here we report the results of a combined ¹⁵⁵Gd Mössbauer and neutron powder diffraction study of GdAgSb₂ that relies on a recently demonstrated large-area flat-plate geometry to overcome the severe absorption problems associated with

Gd-based materials [8]. We confirm that the onset of local magnetic order (using ¹⁵⁵Gd Mössbauer spectroscopy) and long-ranged magnetic order (using neutron diffraction) coincide at $T_N = 13.8(4)$ K. Analysis of the Mössbauer data shows that the Gd moments are ordered perpendicular to the crystallographic *c*-axis, while the neutron diffraction patterns confirm that the magnetic structure is doubled along one of the basal plane axes. These results are in full agreement with those of the earlier resonant x-ray work [7] and anisotropic magnetization data [3].

2. Experimental methods

The single crystal samples used in this study were grown in the Ames Laboratory using the same methods used earlier [3, 7, 9].

The crystals were powdered gently and about 450 mg was used for ¹⁵⁵Gd Mössbauer spectroscopy on a conventional cold-source spectrometer. The 50 mCi ¹⁵⁵Sm source was prepared by neutron activation of about 500 mg of ¹⁵⁴SmPd₃. 98.7% pure ¹⁵⁴Sm metal was arc-melted with a stoichiometric weight of Pd metal under Ti-gettered argon to form the source compound. This was powdered and pressed with aluminium powder and the resulting pellet was activated in the National Research Universal (NRU) research reactor at Chalk River, Ontario. The source and sample were mounted vertically in a helium-flow cryostat and the drive was operated in sine mode. The 86.55 keV γ -photons used for

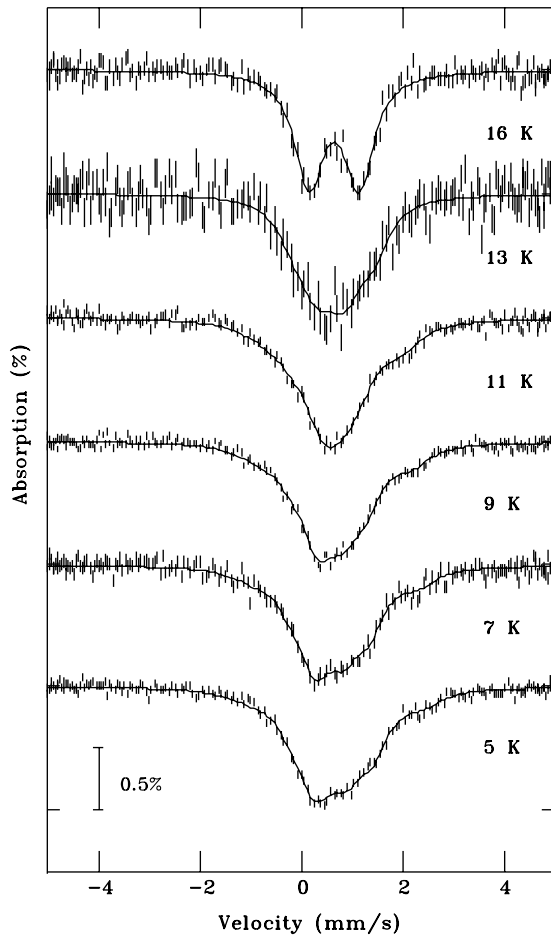


Figure 1. ^{155}Gd Mössbauer spectra of GdAgSb_2 showing the evolution of magnetic splitting on cooling through $T_N = 13.8(4)$ K. Solid lines are fits to a full Hamiltonian solution as described in the text.

^{155}Gd Mössbauer spectroscopy were isolated from the various x-rays emitted by the source using a high-purity Ge detector. Calibration of the spectrometer was achieved using a laser interferometer mounted on the back of the drive. Velocities were cross-checked against $^{57}\text{Co}/\alpha\text{-Fe}$ at room temperature. A calibrated Cernox thermometer was used to monitor the sample temperature and a stability of better than ± 0.01 K was observed. Spectra were fitted using a nonlinear least-squares minimization routine with line positions and intensities derived from an exact solution to the full Hamiltonian [10].

For the neutron diffraction work, 400 mg ($\sim 1/e$ thickness for absorption) was spread across a 2 cm by 8 cm area on a 600 μm thick single crystal silicon wafer and immobilized using a 1% solution of GE-7031 varnish in toluene/methanol (1:1) [8]. Neutron diffraction experiments were carried out on the C2 multi-wire powder diffractometer (DUALSPEC) at the NRU reactor, Canadian Neutron Beam Centre, Chalk River, Ontario. A relatively long neutron wavelength of 2.3672(1) \AA was used so as to access the low-angle ($\frac{1}{2}$ 0 0) magnetic reflection without interference from direct beam contamination. The plate was oriented with its surface normal parallel to the incident neutron beam in order to maximize the total flux onto the sample and the measurements were

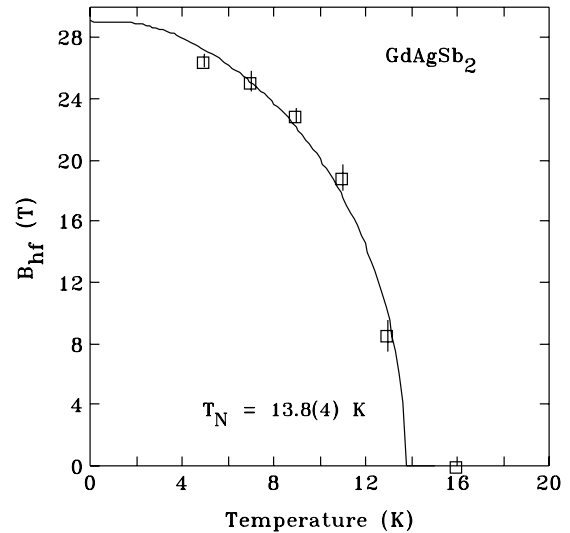


Figure 2. Temperature dependence of the ^{155}Gd Mössbauer hyperfine field (B_{hf}) of GdAgSb_2 showing the Néel temperature to be 13.8(4) K. The solid line is a fit using a $J = \frac{7}{2}$ Brillouin function, appropriate for the Gd^{3+} ion.

made in transmission mode. Temperatures down to 3.6 K were obtained using a closed-cycle refrigerator with the sample in a partial pressure of helium to ensure thermal uniformity. All full-pattern magnetic and structural refinements employed the FullProf/WinPlotr suite [11, 12] with neutron scattering length coefficients for natural Gd taken from the tabulation by Lynn and Seeger [13], as detailed in our previous work on $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ [14]. No absorption correction was applied, however the data were truncated at $2\theta = 60^\circ$ to minimize the impact of angle-dependent absorption effects.

3. Results

3.1. ^{155}Gd Mössbauer spectroscopy

The ^{155}Gd Mössbauer spectrum of GdAgSb_2 at 16 K (above T_N) shown in figure 1 can be fitted as a paramagnetic pattern with an axially symmetric electric field gradient and $eQV_{zz} = 2.09(3)$ mm s^{-1} . On cooling through T_N , a clear magnetic contribution develops and at 5 K the spectrum can be fitted with a hyperfine field (B_{hf}) of 26.5(5) T and an angle (θ) of 90° between B_{hf} and V_{zz} . The $4mm$ point symmetry of the Gd(2c) site in the ZrCuSi_2 -type structure requires that the principal axis of the electric field gradient tensor lie along the crystallographic c -axis, so the observation that $\theta = 90^\circ$ means that the Gd moments must lie in the ab -plane. This provides an independent and local confirmation of the ordering deduced from resonant x-ray scattering [7].

Tracking the temperature dependence of the hyperfine field allows us to determine the ordering temperature to be 13.8(4) K, as shown in figure 2. While this transition temperature is consistent with the 14.0 K originally reported by Solugub *et al* [2] on arc-melted samples, it is somewhat higher than the Néel temperatures found by bulk measurements of single crystals (12.8(1) K [3]) and by xrms (13 K [7]).

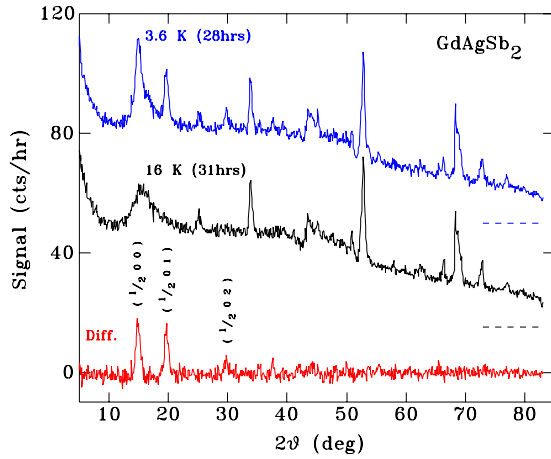


Figure 3. Neutron diffraction patterns taken at 16 K (above T_N) and 3.6 K (well below T_N) showing the additional magnetic reflections that appear as the material orders. The calculated difference pattern shown at the bottom emphasizes the magnetic peaks, the most prominent of which have been indexed. The two measured patterns have been offset vertically for visualization purposes, however the dashed lines at the right show the locations of the actual zero values in each case.

Table 1. Crystallographic data for GdAgSb₂ in the tetragonal $P4/nmm$ space group [3].

Atom	Site	Point symmetry	x	y	z
Gd	2c	$4mm$	$\frac{3}{4}$	$\frac{3}{4}$	0.7641(1)
Ag	2b	$\bar{4}m2$	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
Sb(1)	2c	$4mm$	$\frac{1}{4}$	$\frac{1}{4}$	0.6811(1)
Sb(2)	2a	$\bar{4}m2$	$\frac{3}{4}$	$\frac{1}{4}$	0

3.2. Neutron diffraction

While the neutron diffraction signal from the GdAgSb₂ sample is weak, many nuclear peaks are clearly seen in the 16 K pattern taken above the magnetic ordering temperature (figure 3). The weak scattering signal means that background effects are far more visible, and three clear contributions are apparent in figure 3. Below $2\theta = 10^\circ$ spill-over from the straight-through beam becomes significant, between $2\theta \sim 15^\circ$ and $2\theta \sim 20^\circ$ there is a broad feature due to secondary scattering from detector components, which also leads to a further contribution for $45^\circ < 2\theta < 50^\circ$. The gradual fall-off in the background at higher angles is in large part due to absorption by the increasing effective thickness of the flat plate seen at higher scattering angles.

The atomic position parameters used in our refinement of the neutron diffraction patterns were taken from the work of Myers *et al* [3] and are shown in table 1.

Cooling below T_N leads to the appearance of several new peaks associated with the magnetic ordering. These are especially clear in the difference pattern shown at the bottom of figure 3. These new peaks can be indexed to the original crystallographic cell by a simple doubling of the a -axis, and the first three are marked in figure 3 as $(\frac{1}{2} 0 0)$, $(\frac{1}{2} 0 1)$ and $(\frac{1}{2} 0 2)$. This indexing immediately confirms the cell

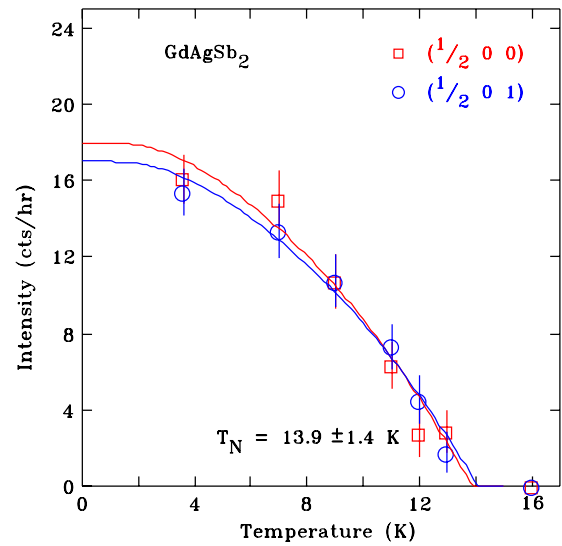


Figure 4. Intensities of the $(\frac{1}{2} 0 0)$ and $(\frac{1}{2} 0 1)$ peaks for GdAgSb₂ as functions of temperature showing an average Néel temperature of 13.9 ± 1.4 K. The solid lines are fits to squared $J = \frac{1}{2}$ Brillouin functions (the intensity is proportional to the moment squared).

doubling deduced from the resonant x-ray scattering work [7] and places the gadolinium moments in the ab -plane. We note here that the tetragonal symmetry of the $P4/nmm$ space group places significant limits on what we can determine about the magnetic structure. As the a - and b -directions are completely equivalent they cannot be distinguished in a powder diffraction experiment. This means that we cannot tell the difference between the Gd moments being ordered parallel to the b -axis (as is implied by the indexing in figure 3) or parallel to the a -axis (which would make the indices $(0 \frac{1}{2} 0)$, $(0 \frac{1}{2} 1)$ and $(0 \frac{1}{2} 2)$). Unfortunately the ¹⁵⁵Gd Mössbauer data cannot be used to distinguish between these two cases either as the axially symmetric electric field gradient tensor (itself a consequence of the tetragonal symmetry) also makes it impossible to determine the direction of the Gd moments within the ab -plane.

As with the Mössbauer hyperfine field, tracking the intensities of the two strongest magnetic reflections in figure 4 yields an estimate of the ordering temperature as 13.9 ± 1.4 K, somewhat less precise than the Mössbauer value in figure 2 because the peaks are quite weak, however it is fully consistent with it. In particular, there is a clear magnetic signal present at 13 K in both the Mössbauer data (figure 1) and the neutron diffraction pattern (figure 4), strongly suggesting that the Néel temperature is slightly above 13 K. The origin of the small (~ 0.8 K) discrepancy between the current determinations and that previously made using x-ray resonant exchange scattering [7] is unknown at this time, but we emphasize that in all other respects, we are in full agreement with the previously reported magnetic structure.

The refinement of the diffraction pattern obtained at 3.6 K is shown in figure 5. The lattice parameters were fixed to the values obtained from the refinement of the nuclear pattern taken at 16 K. As shown in the difference plot (figure 3), the antiferromagnetic order of the Gd sublattice leads to two clear peaks at $2\theta = 15.9^\circ$ and $2\theta = 20.6^\circ$, which correspond

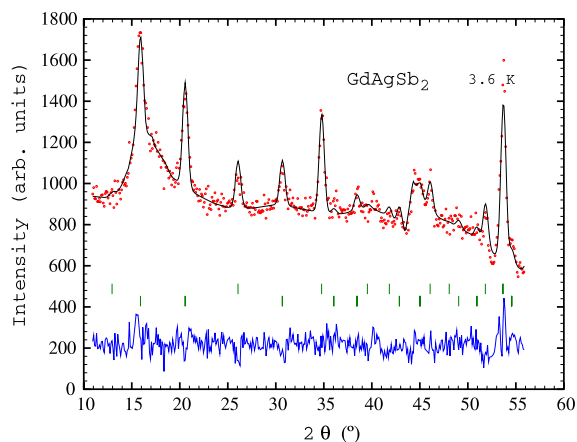


Figure 5. Refined diffraction pattern for GdAgSb₂ obtained at 3.6 K. The lattice parameters of $a = 4.277(4)$ Å and $c = 10.498(5)$ Å were taken from the nuclear-only pattern at 16 K. The solid line is a full-profile refinement of the nuclear and magnetic contributions. Two rows of Bragg markers are shown (top) nuclear contribution (bottom) magnetic contribution. The residuals are plotted at the bottom of the figure.

to the $(\frac{1}{2} 0 0)$ and $(\frac{1}{2} 0 1)$ reflections, respectively. A third, weaker, magnetic reflection can be seen at $2\theta = 30.7^\circ$ which corresponds to the $(\frac{1}{2} 0 2)$ reflection. The observation of this cell doubling along a tetragonal axis has also been seen in TbAgSb₂, DyAgSb₂ and ErAgSb₂ by André *et al* [6].

In full agreement with the resonant x-ray work of Song *et al* [7], we obtained the best refinement to the 3.6 K pattern by using a $[\frac{1}{2} 0 0]$ propagation vector with the Gd magnetic moments oriented in the tetragonal basal plane, transverse to the propagation vector. The refined Gd moment at 3.6 K is $6.2(3) \mu_B$. As noted above, the tetragonal crystal symmetry makes it impossible to distinguish ordering along the a -axis with doubling of the b -axis, from ordering along the b -axis with doubling of the a -axis.

4. Conclusions

We have demonstrated that neutron powder diffraction can indeed be performed on Gd-based compounds at thermal wavelengths and that it readily yields data of sufficient quality to enable a magnetic structure determination.

Both ¹⁵⁵Gd Mössbauer spectroscopy and thermal neutron powder diffraction confirm that the Néel temperature of GdAgSb₂ is 13.8(4) K and the Gd moments lie in the tetragonal ab -plane. Analysis of the neutron diffraction pattern at 3.6 K shows that the magnetic cell is doubled along one of the basal axes and that the $6.2(3) \mu_B$ Gd moments are ordered within

the basal plane but oriented perpendicular to the doubling direction. These results confirm and extend the description of the magnetic ordering derived by Song *et al* from x-ray resonant exchange scattering measurements [7].

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