

Neutron powder diffraction determination of the magnetic structure of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$

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The $\text{R}_3\text{T}_4\text{X}_4$ family (R = rare earth, T = Cu, Ag, Au, and X = Si, Ge, Sn) form an extensive series of isostructural compounds which exhibit a rich variety of magnetic ordering. They crystallize in the orthorhombic $\text{Gd}_3\text{Cu}_4\text{Ge}_4$ -type structure (space group *Immm*, #71) [1] in which the R atoms occupy two crystallographic sites (2d and 4e), the T atoms occupy the 8n site and the X atoms occupy two equi-populous sites (4f and 4h). In general, the R moments order antiferromagnetically, often with quite different moment values and with distinct magnetic structures adopted by the two R sublattices. In some cases the two R sublattices will also have quite different ordering temperatures [2].

Mazzone *et al.* [3] observed magnetic ‘events’ at 22 K and 8 K in ac-susceptibility measurements on $\text{Gd}_3\text{Ag}_4\text{Sn}_4$, and the magnetization curve, obtained at 5 K, suggested purely antiferromagnetic ordering of the Gd sublattices. Voyer *et al.* [4] used ^{119}Sn Mössbauer spectroscopy to show that the magnetic ordering temperature of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ is in fact 28.8(2) K, and that the 8 K event is most likely a 90° spin-reorientation.

We have demonstrated the extremely productive complementarity of Mössbauer spectroscopy (*a local probe*) and neutron diffraction (*an extended probe*) [5, 6] and it would be desirable to carry out a neutron powder diffraction study of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ to complement our previous ^{119}Sn Mössbauer work. However, studies of Gd containing materials are challenging due to natural Gd being the strongest neutron-absorbing element in the Periodic Table ($\sigma_{\text{abs}} = 49700$ b at a neutron wavelength of 1.80 Å).

Neutron diffraction measurements were made using the C2 multi-wire powder diffractometer at Chalk River Laboratories, Ontario, at a wavelength of 2.37211(16) Å. The extreme absorption cross section of natural Gd leads to a 1/e thickness of about 14 μm for $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ at the wavelength used here. Approximately 300 mg of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ was spread on a 600 μm single-crystal silicon plate, to cover an area of 8 cm by 2.4 cm, and immobilised using highly diluted (1% by wt.) GE-7031 varnish [7]. The plate was oriented with its surface normal parallel to the incident neutron beam in order to maximise the total flux onto the sample. Refinements of the neutron diffraction patterns employed the FullProf/WinPlotr suite [8, 9] and the magnetic structures were drawn using the FP-Studio package. Representational Analysis was carried out using the SARA*h* program [10].

The effects of the magnetic ordering of the Gd sublattices are

clear in Fig. 1, especially in the 2θ range 12–22°.

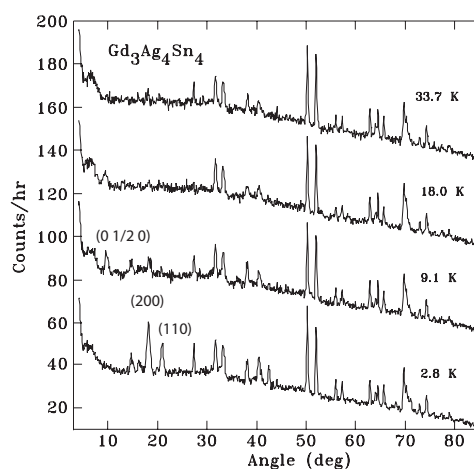


Fig 1. Neutron diffraction patterns of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ obtained with a neutron wavelength of $\lambda = 2.37211(16)$ Å.

The three principal magnetic contributions are indexed as $(0\frac{1}{2}0)$, (200) and (110), as indicated in Fig. 1, and the temperature dependence of their integrated areas are shown in Fig. 2. The purely magnetic $(0\frac{1}{2}0)$ peak appears at the magnetic ordering temperature, reaches its maximum intensity at around 12 K and then decreases sharply below 9 K, disappearing by about 7 K. Consistent with this behaviour, we see substantial increases in the intensities of both the (200) and (110) peaks, starting at around 12 K. The presence of the $(0\frac{1}{2}0)$ peak for $28\text{K} > T > 7\text{K}$ indicates that the magnetic ordering of at least one of the Gd sublattices involves a cell doubling along the crystal b-axis, i.e. a propagation vector $k_1 = [0\frac{1}{2}0]$. More complete analysis shows that the $(0\frac{1}{2}0)$ peak is due to ordering of the Gd(4e) sublattice.

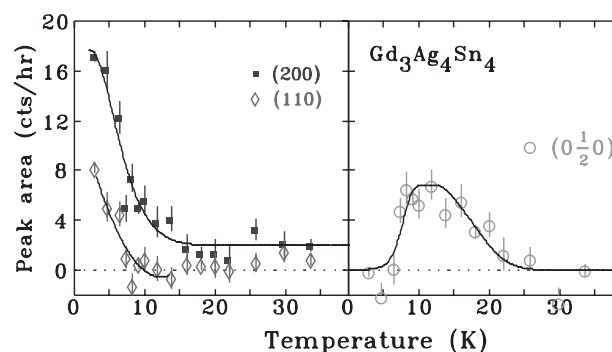


Fig 2. Temperature dependences of the (200), (110) and $(0\frac{1}{2}0)$ peak areas of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$.

The magnetic contribution at 2.8 K is clear in Fig. 1. Besides the $k_2 = [0\ 0\ 0]$ magnetic contributions to (200) and (110) we also see additional, purely magnetic peaks, two of which are quite prominent on the lower-angle side of the (200) peak (marked with asterisks in Fig. 3 and appearing at $2\theta = 14.5^\circ$ and 16.0°). These two peaks are incommensurate with the $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ crystal lattice and are also present in the 9.1 K pattern.

Given that there are two Gd magnetic sublattices in $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ and clear magnetic contributions at both commensurate and incommensurate positions in the 2.8 K diffraction pattern we can associate one Gd site with the commensurate magnetic order and the other site with the incommensurate magnetic order.

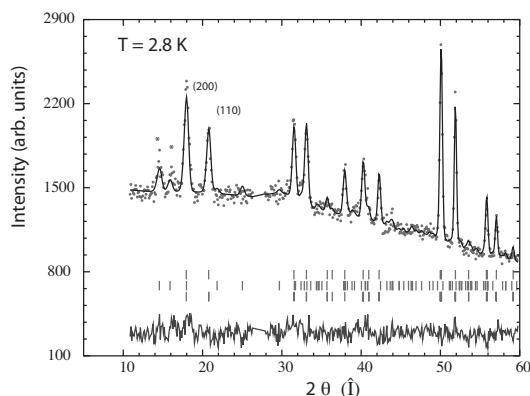


Fig 3. Refined neutron diffraction pattern of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ obtained at 2.8 K. The Bragg markers are (top) nuclear phase, (middle) Gd(2d) magnetism and (bottom) Gd(4e) magnetism. Incommensurate peaks are marked with asterisks.

The best match to the observed (200):(110) intensity ratio is with the Gd(4e) sites ordered antiferromagnetically (+ -) along the crystal c-axis, (Fig. 4). The magnitude of the Gd(4e) magnetic moment at 2.8 K is $6.8\ \mu_B$. In Fig. 3 we show the refinement of the neutron diffraction pattern obtained at 2.8 K.

The presence of a purely magnetic $(0\ \frac{1}{2}\ 0)$ peak in the temperature range 7 K to 28 K, whose disappearance coincides with the development of substantial magnetic contributions to the (200) and (110) peaks, suggests that the doubling involves the Gd(4e) site. The best match to the observed $(0\ \frac{1}{2}\ 0)$ intensity at 9.1 K is with the Gd(4e) sites ordered in the *ab*-plane and making an angle of about 20° with the crystal a-axis.

With the ordering of the Gd(4e) site determined to be commensurate, we attribute the presence of purely magnetic incommensurate peaks in the temperature range 3–12 K to the Gd(2d) site. A tentative search for a suitable propagation vector to describe the incommensurate magnetic order of the Gd(2d) sublattice was carried out using *k* search, from the FullProf/WinPlotr package [8, 9]. One possible solution is $k = [0.43, 0.19, 0]$. Representational Analysis followed by refinement of the 2.8 K pattern yields a structure in which $6.5\ \mu_B$ Gd(2d) moments are aligned along the crystal c-axis.

In Fig. 4 we show the magnetic structure of the Gd(4e) sublat-

tice both below the spin-reorientation temperature ($T_{sr} \sim 8\ \text{K}$) and above. The determination of the Gd(2d) order is not as definitive as the Gd(4e) order so it is not shown in Fig. 4.

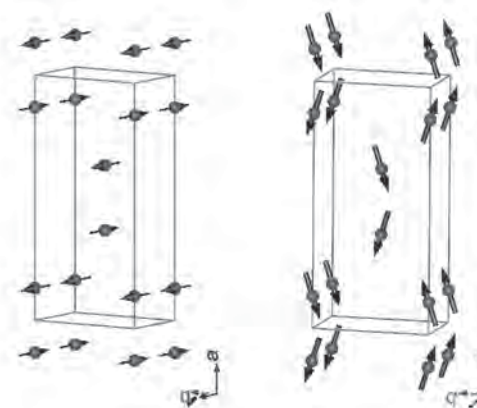


Fig 4. Magnetic structures of the Gd(4e) sublattice in $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ below and above the spin-reorientation temperature (T_{sr}). The view is of the *ab*-plane, tilted slightly. The *a*-axis is vertical, as indicated by the arrow.

Our neutron diffraction work confirms the 28 K ordering temperature initially determined by ^{119}Sn Mössbauer spectroscopy and clearly shows that the magnetic order of the Gd(4e) sublattice does indeed undergo a 90° reorientation from planar to axial upon cooling though 9 K. The independent support that data from each technique provides to the other underlines the rich complementarity of Mössbauer spectroscopy and neutron diffraction in studying magnetic ordering.

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References

- [1] Rieger W 1970 *Monatsch. Chem.* 101 449–62.
- [2] Ryan D H, Cadogan J M, Voyer C, Napolitano M, Riani P and Cranswick L M D 2008 *Hyp. Int.* to be published.
- [3] Mazzone D, Riani P, Napolitano M and Canepa F 2005 *J. Alloys and Compounds* 387 15–9.
- [4] Voyer C J, Ryan D H, Napolitano M and Riani P 2007 *J. Phys.: CM* 19 156209 (10 pp).
- [5] Ryan D H, Cadogan J M, Gagnon R and Swainson I P 2004 *J. Phys.: CM* 16 3183–98.
- [6] Perry L K, Cadogan J M, Ryan D H, Canepa F, Napolitano M, Mazzone D and Riani P 2006 *J. Phys.: CM* 18 5783–92.
- [7] Ryan D H and Cranswick L M D 2008 *J. Appl. Cryst.* 41 198–205.
- [8] Rodríguez-Carvajal J 1993 *Physica B* 192 55–69.
- [9] Roisnel T and Rodríguez-Carvajal J 2001 *Mater. Sci. Forum* 378–81 118–23.
- [10] Wills A S 2000 *Physica B* 276–8 680–1