

# Neutron Diffraction and $^{119}\text{Sn}$ Mössbauer Study of $\text{Sm}_3\text{Ag}_4\text{Sn}_4$

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The ternary rare earth compound family  $\text{R}_3\text{T}_4\text{X}_4$  (where R is a rare earth, T = Cu, Ag, Au, and X = Si, Ge, Sn) have been extensively studied due to their rich variety of magnetic behaviour [1–5]. They crystallize in the orthorhombic  $\text{Gd}_3\text{Cu}_4\text{Ge}_4$ -type structure (space group  $Immm$ , #71) [6], with the rare earth atoms occupying two crystallographically distinct sites (2d and 4e), the transition metal (T) on the 8n site and the X atoms filling the 4f and 4h sites.

One interesting complication in the  $\text{R}_3\text{T}_4\text{X}_4$  family derives from the difficulty in unambiguously determining the ordering temperature from simple bulk magnetic measurements (magnetisation and susceptibility). In some cases, the signal from the initial ordering is weak or absent, and a subsequent magnetic reorientation provides a more definitive marker, leading to the misidentification of the ordering temperature [1]. Where neutron diffraction data are available, this error is readily corrected. However, for Sm- and Gd-based compounds, the high absorption cross-section makes neutron-based methods challenging and they are rarely attempted.

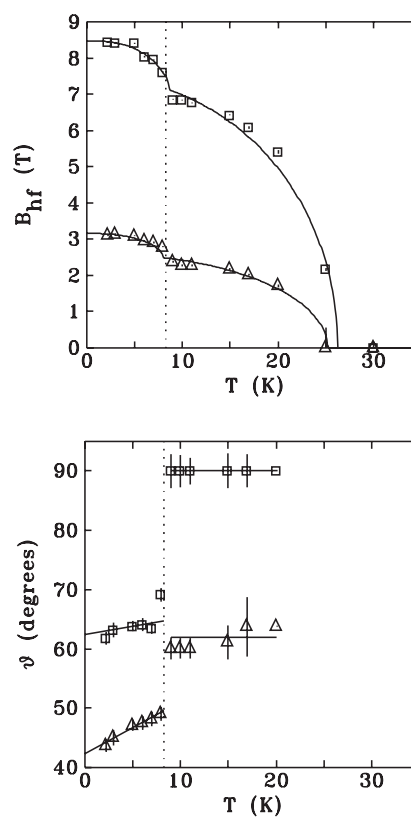
Neutron diffraction measurements were made using the C2 multi-wire powder diffractometer at Chalk River Laboratories, Ontario, at a wavelength of 2.3719 Å. The very large absorption cross section in Sm ( $\sigma_{abs} = 5922(56)$  barn) leads to a  $1/e$  absorption thickness of  $\sim 140$   $\mu\text{m}$  for  $\text{Sm}_3\text{Ag}_4\text{Sn}_4$  and so precludes mounting in a conventional 5 mm diameter cylindrical sample holder. We therefore used a large-area flat-plate holder with single crystal silicon windows that was developed to work with highly absorbing samples [7]. This holder allowed us to place about 1.6 g of sample in the 8 cm  $\times$  2.4 cm beam and obtain a usable scattering signal. Cooling was achieved using a closed-cycle refrigerator.

From our fits to  $^{119}\text{Sn}$  Mössbauer spectra we obtain the temperature dependence of  $\mathbf{B}_{hf}$  for each site and the corresponding angle  $\vartheta$  between  $\mathbf{B}_{hf}$  and  $\mathbf{V}_{zz}$  (Figure 1). These yield a transition temperature of  $T_N = 26.0(5)$  K and a spin reorientation temperature of 8.3(3) K.

Only the lower event was seen previously in susceptibility data and it was identified as the onset of bulk order [8], however this assignment is clearly incorrect.

The small sample combined with the large absorption cross-section of natural samarium leads to relatively weak scattering. The situation is exacerbated by both the very small coherent scattering length for Sm (0.00(5) fm), which will lead

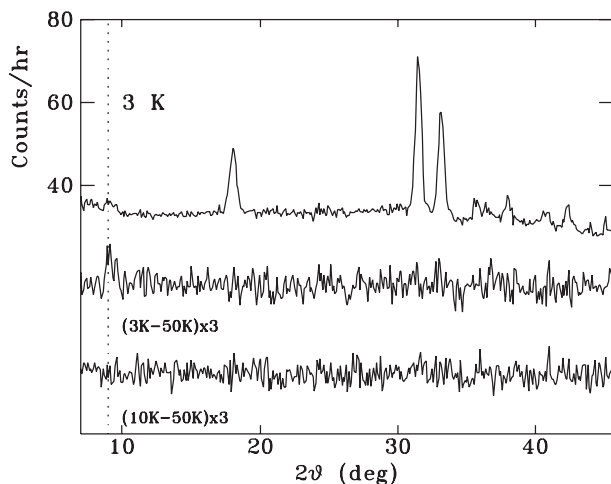
to reduced structural scattering, and by the small magnetic moment ( $\sim 0.5 \mu_B$ ) expected on the Sm atoms in metallic compounds [9–11], which will yield very weak magnetic scattering. Long counting times (several days) were required to obtain useful data.



**Fig 1.** (Top): Temperature dependence of the hyperfine field  $B_{hf}$  in  $\text{Sm}_3\text{Ag}_4\text{Sn}_4$  fitted with a sum of two  $J = 5/2$  Brillouin functions. (bottom): The angle ( $\vartheta$ ) between  $\mathbf{V}_{zz}$  and  $\mathbf{B}_{hf}$ . Solid lines are guides to the eye.

Examination of the 3 K diffraction pattern, shown at the top of Figure 2, shows no striking change from the paramagnetic state, although a weak peak near  $2\vartheta = 9^\circ$  is visible. The magnetic scattering can be isolated by taking the difference between the patterns at 3 K and 50 K (middle curve in Figure 2) and we see that the only significant magnetic signal is associated with the  $9^\circ$  peak, which can be identified as being due to the (100) reflection. The width of this peak is consistent with both the instrumental resolution function and the structural peaks at higher angles, leading us to conclude that long ranged magnetic order is definitely established at 3 K in this compound. Furthermore, the presence of this (100) peak

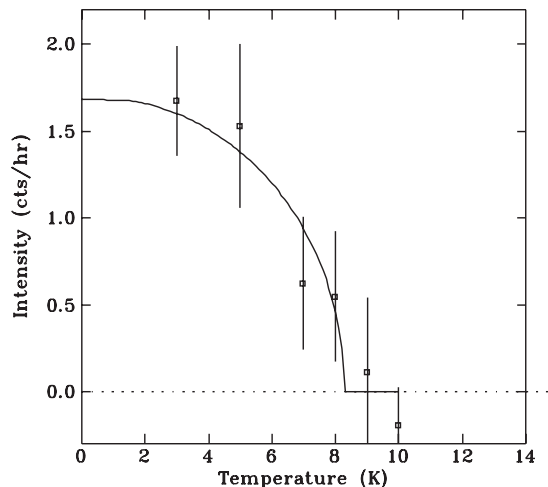
indicates that the Sm moments have at least some component in the bc-plane.



**Fig 2.** Top: Neutron diffraction pattern for  $\text{Sm}_3\text{Ag}_4\text{Sn}_4$  taken at 3 K showing a weak magnetic peak at  $2\theta = 9^\circ$  (dotted line). Middle: difference between the 3 K and 50 K patterns (scaled by a factor of 3) to emphasise the magnetic peak. Bottom: difference between the 10 K and 50 K patterns enlarged by the same factor of 3, showing no apparent magnetic signal. All measurements were made at a wavelength of 2.3719 Å.

To determine the magnetic structure  $\text{Sm}_3\text{Ag}_4\text{Sn}_4$  at 3 K, we considered the 16 magnetic space groups associated with the  $Immm$  (#71) crystallographic space group. Only two ( $I_pmmm'$  and  $I_pmm'm$ ) yield enough intensity on the (100) peak to be consistent with the data shown in Figure 2. Remarkably, neither of these groups permit magnetic ordering at the 2d site, setting  $\text{Sm}_3\text{Ag}_4\text{Sn}_4$  apart from the vast majority of compounds in the  $\text{R}_3\text{T}_4\text{X}_4$  family where ordering on the 2d site is either the only form seen, or at least the preferred ordering, with the 4e sites ordering only at a much reduced temperature.

Tracking of the intensity of the  $9^\circ$  peak with temperature (Figure 3), shows that it disappears at 8.3(4) K in perfect agreement with the reorientation temperature measured by  $^{119}\text{Sn}$  Mössbauer spectroscopy. It is clear from the bottom curve in Figure 2 that no significant magnetic signal is observed at 10 K, despite clear evidence in the Mössbauer spectra that the compound remains ordered until 26 K. Simulation of the nine possible magnetic groups that support AF ordering of the samarium moments reveals that only the two candidate groups for the low temperature structure ( $I_pmmm'$  and  $I_pmm'm$ ) yield a strong magnetic signature, the others all lead to multiple weak magnetic peaks. As a result, our failure to detect magnetic scattering above 9 K does not necessarily demand a loss of magnetic order at 8.3(4) K, but rather, when taken with the clear magnetic signal in the  $^{119}\text{Sn}$  Mössbauer spectra, it implies a change in magnetic order, with the Sm moments rotating closer to the a-axis. The overall weakness of the magnetic scattering, and the absence of magnetic peaks at 10 K precludes further analysis of the neutron diffraction data, and we are unable to determine the magnetic structure between 8.3 and 26.0 K.



**Fig 3.** Temperature dependence of the intensity of the (100) reflection at  $2\theta = 9^\circ$ . The solid line is a Brillouin function fit and the transition temperature derived from the fit, 8.3(4) K, is in excellent agreement with the moment reorientation temperature obtained from  $^{119}\text{Sn}$  Mössbauer spectroscopy.

$^{119}\text{Sn}$  Mössbauer spectroscopy and neutron diffraction provide distinct yet complementary information on the magnetic ordering in  $\text{Sm}_3\text{Ag}_4\text{Sn}_4$ , which can be used to refine the choice of magnetic space groups ( $I_pmmm'$  or  $I_pmm'm$ ). Analysis of the magnetic environments of the two tin sites shows that only the  $I_pmmm'$  group yields a non-zero transferred hyperfine field at both tin sites. Rietveld refinement of the 3 K pattern, assuming that the  $I_pmmm'$  structure is correct, then yields a samarium moment of  $0.47 \pm 0.10 \mu_B$  on the Sm 4e site.

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