Hyperfine Interact
DOI 10.1007/s10751-011-0416-3

^{155}Gd Mössbauer investigation of the magnetic order and spin-reorientation in $Gd_3Ag_4Sn_4$

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Abstract In a recent study of the magnetic order in $Gd_3Ag_4Sn_4$ by neutron powder diffraction and ^{119}Sn Mössbauer Spectroscopy we showed that both the Gd(2d) and Gd(4e) sublattices order antiferromagnetically at 28.8(2) K. We also demonstrated that the 'magnetic event' around 8 K is in fact a 'plane to axis' spin-reorientation of the Gd magnetic structure. Here, we extend our study with ^{155}Gd Mössbauer Spectroscopy. The initial magnetic ordering at 30(2) K is clear for both sites and substantial changes in the hyperfine fields are observed at 8 K when the magnetic structure reorients.

Keywords Magnetic order · Spin-reorientation · Mössbauer Spectroscopy

1 Introduction

The $R_3T_4X_4$ family (R = rare earth, T = Cu, Ag, Au, Mn, Pd, and X = Si, Ge, Sn) crystallize in the orthorhombic $Gd_3Cu_4Ge_4$-type structure (space group *Immm*, #71) [1] in which the R atoms occupy two crystallographic sites (4e and 2d), the transition metal (T) occupies the 8n site and X occupies the 4f and 4h sites. In general, the R moments order antiferromagnetically, often with quite different moment values, and with distinct magnetic structures adopted by the two R sublattices. We refer the reader to our recent review of the magnetism of the $R_3T_4X_4$ compounds [2] for further details.

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Published online: 27 October 2011

The magnetism of $Gd_3Ag_4Sn_4$ was first studied by Mazzone et al. [3] who observed magnetic 'events' at 22 K and 8 K in ac-susceptibility measurements. The 22 K 'event' was quite broad and could be suppressed by an applied field of 1 T. Magnetization data obtained at 5 K suggested a purely antiferromagnetic ordering of the Gd sublattices at a Néel temperature of 8 K.

In a previous paper [4] we used ^{119}Sn Mössbauer spectroscopy to show that the magnetic ordering temperature of $Gd_3Ag_4Sn_4$ is in fact 28.8(2) K. The sudden changes in the temperature dependences of the transferred hyperfine fields at the two Sn sites, evident in the ^{119}Sn spectra were interpreted in terms of the 8 K 'event' observed by Mazzone et al. [3] being a spin-reorientation of the Gd magnetic order, rather than a magnetic ordering of one of the Gd sublattices.

We subsequently determined the magnetic structures of the two Gd sublattices in $Gd_3Ag_4Sn_4$ by neutron powder diffraction [5]. We confirmed that the onset of long-range magnetic ordering is in accord with our ^{119}Sn Mössbauer results. At 2.8 K the Gd(4e) sublattice is antiferromagnetically ordered along the crystal *c*-axis, commensurate with the crystal lattice. The Gd(2d) sublattice is also ordered along the *c*-axis but its magnetic structure is incommensurate. Finally, our neutron diffraction work showed that the magnetic order of the Gd(4e) sublattice does indeed undergo a 90° reorientation from planar to axial on cooling. It is conceivable that magnetic exchange is sufficient to keep the two Gd sublattices collinear. Thus, the Gd(2d) would also undergo a 90° reorientation from planar to axial. This would be fully consistent with our ^{119}Sn Mössbauer work but we were unable to provide definitive proof of this suggestion on the basis of neutron diffraction.

Here, we present the results of our ^{155}Gd Mössbauer study of the local magnetism of the two Gd sites in $Gd_3Ag_4Sn_4$. Our ^{155}Gd results confirm the nature of the spin-reorientation of the magnetic order described above.

2 Experimental methods

The $Gd_3Ag_4Sn_4$ sample used in this study was the same sample used in our previous neutron diffraction [5] and ^{119}Sn Mössbauer [4] work and a detailed description of the sample preparation and characterisation can be found in our previous paper [5]. About 450 mg of powder and a 50 mCi $^{155}SmPd_3$ source were mounted vertically in a conventional cold-source spectrometer operated in sine-mode. The 86.55 keV ^{155}Gd Mössbauer $\gamma-$photons were isolated from the various x-rays emitted by the source using a high-purity Ge detector. The spectrometer's drive system was calibrated using a laser interferometer and velocities were cross-checked against ^{57}Co**Rh**/$\alpha-$Fe at room temperature. The ^{155}Gd Mössbauer spectra were fitted using a non-linear least-squares minimisation routine with line positions and intensities derived from an exact solution to the full Hamiltonian [6].

3 Results and discussion

Figure 1 shows the ^{155}Gd Mössbauer spectra of $Gd_3Ag_4Sn_4$ obtained between 30 K (above T_N) and 1.9 K. At 30 K the spectrum showed no signs of a magnetic hyperfine field at either site, as expected from our ^{119}Sn Mössbauer work [4], and

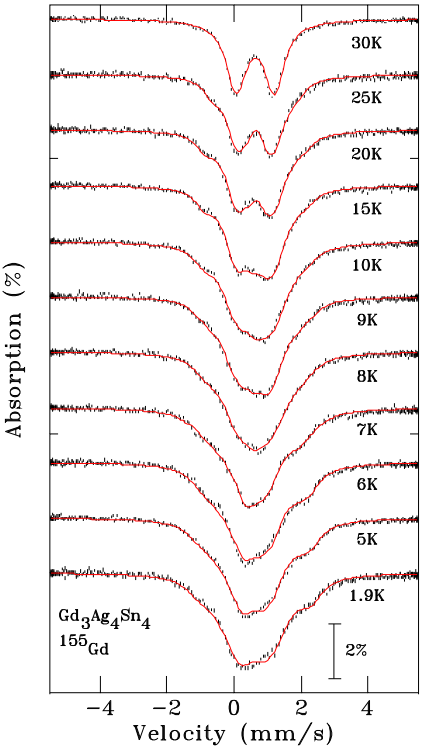

Fig. 1 ^{155}Gd Mössbauer spectra of $Gd_3Ag_4Sn_4$ showing the evolution of magnetic splitting upon cooling. The *solid lines* are fits to a full Hamiltonian solution as described in the text

we obtained values of 2.22(3) mm/s and 2.85(6) mm/s for the magnitude of the quadrupole splitting parameter eQ_gV_{zz} at the Gd(2d) and Gd(4e) sites, respectively. These values were then fixed for the magnetic spectra. The point symmetries of the Gd(2d) and Gd(4e) sites are *mmm* and *2 mm*, respectively, which require only that the principal axes of the electric field gradient (EFG) tensors at the two Gd sites lie along crystallographic axes, but do not permit an assignment of those axes. Furthermore, the strong line overlap at 1.9 K apparent in Fig. 1 made an independent determination of the asymmetry parameters (η) unreliable, we were therefore guided by the ^{170}Yb study of isostructural $Yb_3Cu_4Ge_4$ by Dhar et al. [7], who showed that the EFG at the Yb(2d) site "has a strong non-axial character" whereas that at the Yb(4e) site "has an axial character". Following a search over possible choices of η and the angle ϑ between eQ_gV_{zz} and B_{hf}, we found that $\eta(2d) = 1$ and $\eta(4e) = 0$ provided a self-consistent description of the magnetic spectra over the temperature range covered here (Fig. 1).

A clear magnetic splitting develops on cooling through T_N, and a fit to the temperature dependence of the hyperfine fields at the two Gd sites (B_{hf}^{2d} and B_{hf}^{4e}) yields an average Néel temperature of $T_N = 30(2)$ K (Fig. 2). We also show the angle between the hyperfine field and the principal axis of the EFG. Both Gd sites order together at T_N and the effects of the spin-reorientation at ~8 K are clear. Above 8 K, the Gd(2d) site orders with its hyperfine field perpendicular to its local EFG z-axis whereas the Gd(4e) site orders at 20° from its local EFG z-axis. Below the

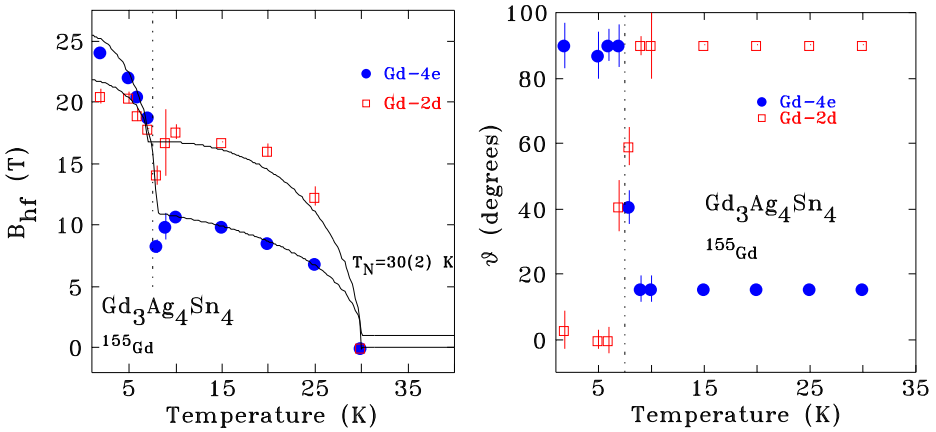

Fig. 2 Temperature dependences of the ^{155}Gd hyperfine magnetic fields (*left*) and the angle ϑ between the hyperfine field and the local EFG z-axis (*right*) at the two Gd sites

spin-reorientation transition, B_{hf}^{2d} is parallel to the local local EFG z-axis and B_{hf}^{4e} is perpendicular to it.

4 Conclusions

We have used ^{155}Gd Mössbauer spectroscopy to investigate the magnetic spin-reorientation in $Gd_3Ag_4Sn_4$. Our results confirm those in our previous neutron diffraction study. The magnetic ordering temperature derived from ^{155}Gd Mössbauer is 30(2) K, consistent with our earlier value of 28.8(2) K derived from ^{119}Sn Mössbauer data [4]. Our neutron diffraction data suggested that the magnetic 'event' previously observed at ~8 K is, in fact, a 'plane to axis' spin-reorientation of the Gd magnetic structure upon cooling. This conclusion is consistent with our previous ^{119}Sn Mössbauer spectroscopy work and is further confirmed here by ^{155}Gd Mössbauer spectroscopy.

Acknowledgements J. M. Cadogan acknowledges support from the Canada Research Chairs programme. Financial support for various stages of this work was provided by the Natural Sciences and Engineering Research Council of Canada and Fonds Québécois de la Recherche sur la Nature et les Technologies. We gratefully acknowledge the assistance of Raghu Rao and Robert Speranzini in arranging for the activation of the ^{155}Gd Mössbauer source in the National Research Universal (NRU) research reactor, which is operated by Atomic Energy of Canada, Ltd., at Chalk River, Ontario.

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