

Magnetic ordering in $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ and $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ studied using ^{119}Sn Mössbauer spectroscopy

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Abstract

The magnetic properties of $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ and $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ have been investigated using ^{119}Sn Mössbauer spectroscopy. We find that the Néel temperature (T_N) for $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ is 28.8(2) K, much higher than previously reported and fully consistent with de Gennes scaling for the $\text{R}_3\text{T}_4\text{Sn}_4$ ($T = \text{Cu}, \text{Ag}$) compound series. The 8 K event previously identified as T_N is most likely a spin reorientation transition. By contrast, T_N for $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ is confirmed to be anomalously low at only 13.6(1) K, consistent with earlier specific heat data. The sub-splitting of the ^{119}Sn Mössbauer spectrum for $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ at 1.55 K points to a complex magnetic structure, but we find no evidence for the lower-temperature events that are apparent in susceptibility data.

1. Introduction

The orthorhombic $\text{R}_3\text{T}_4\text{X}_4$ family (where R is a rare earth, $T = \text{Cu}, \text{Ag}, \text{Au}$, and $X = \text{Si}, \text{Ge}, \text{Sn}$) represents an extensive series of isostructural compounds that exhibits a rich variety of magnetic ordering. They crystallize in an orthorhombic $\text{Gd}_3\text{Cu}_4\text{Ge}_4$ -type structure (space group $Immm$, #71) [1]. The rare-earth atoms occupy two crystallographically distinct sites (4e and 2d), with the transition metal (T) on the 8n site and X occurring on two equipopulous sites (4f and 4h). In general, the rare-earth moments order antiferromagnetically (AF), often with quite different moment values [2–6], and with distinct magnetic structures adopted by the two rare-earth sublattices. In some cases the two rare-earth sites will also have quite different ordering temperatures [7].

As systematic data on the $\text{R}_3\text{T}_4\text{X}_4$ systems have accumulated, a puzzle has emerged. These materials form intimately related isostructural series for a given choice of T and X, yet several workers have noted the failure of the observed transition temperatures to follow the expected

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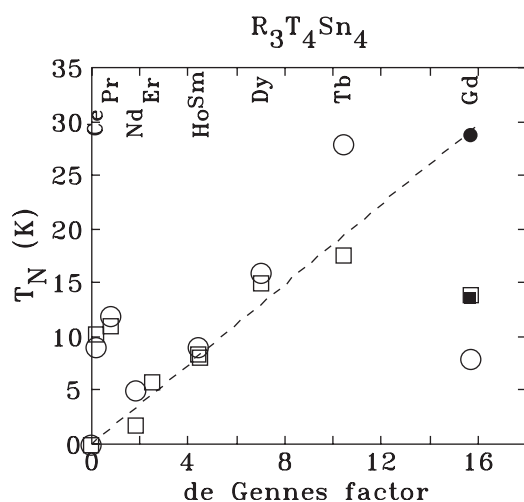


Figure 1. Scaling of ordering temperatures in $R_3Cu_4Sn_4$ (\square) and $R_3Ag_4Sn_4$ (\circ) with the de Gennes factor of the rare earth. The two solid symbols are for this work, while the values plotted as open symbols are taken from: copper series [2, 7–9, 13]; silver series [5, 6, 11, 14, 15]. See text for discussion of the outliers.

scaling with the de Gennes factor in both the $R_3Cu_4Sn_4$ [2, 8–10] and $R_3Ag_4Sn_4$ [5, 11] series. It is tempting to invoke an exotic mechanism to explain this scaling failure, especially in light of the complex and even independent ordering of the two rare-earth sublattices. However, such an approach may miss the real cause of the failure and could also lead to the wrong series members being identified as the anomalous elements.

We believe that the apparent scaling failure may have at its origin a simple but flawed choice of the Gd compounds as reference points. To illustrate this, we show in figure 1 the scaling behaviour observed if one ignores the two Gd compounds entirely. Overall, de Gennes scaling works quite well, with the cerium and praseodymium compounds as obvious outliers. The light rare earths often fail to follow the same scaling as the heavy rare earths [12], and specific heat measurements on $Ce_3Cu_4Sn_4$ [13] and $Pr_3Cu_4Sn_4$ [8] show evidence for complex ordering (Ce) and significant contributions from nearby crystal field split levels (Pr) that likely play a role in the scaling failure. The striking outlier from the heavy rare-earth group is $Tb_3Ag_4Sn_4$ [14] but this system undergoes a coupled magnetostructural transition and the ordering is therefore far from conventional.

With the five outliers removed from consideration, it is the two gadolinium compounds (plotted as open symbols at a de Gennes factor of 15.75 in figure 1) that emerge as clear anomalies. As Gd alloys typically have the highest ordering temperatures of an isostructural rare-earth series, by virtue of gadolinium's maximal de Gennes factor, it is common practice to establish the expected scaling behaviour by joining the Gd point to the origin. This strategy appears to be a spectacular failure here. Two possible explanations for the Gd anomaly are possible: (1) the reported transition temperatures are incorrect, or (2) the two gadolinium compounds are indeed different.

Before considering the second possibility, we must eliminate the first. Ordinarily this would not be an issue as, for most systems, reliable values are readily obtained by susceptibility, magnetization or neutron diffraction. However, here we have complex antiferromagnetic ordering which, as we will show below, makes the interpretation of magnetic data somewhat subjective. In addition, the extreme neutron absorption cross section of ^{157}Gd , which constitutes

nearly 16% of natural Gd, makes neutron diffraction effectively impossible, without resorting to isotopically separated material. We turn therefore to ^{119}Sn Mössbauer spectroscopy, and exploit the transferred hyperfine fields from the Gd moments as a somewhat indirect but phase-quantitative probe of the ordering behaviour. Tin has no magnetic moment, so that any hyperfine field (B_{hf}) observed in a ^{119}Sn Mössbauer spectrum must be due to ordered Gd moments on neighbouring sites. Both tin sites in the $\text{R}_3\text{T}_4\text{Sn}_4$ structure have neighbours from each of the two R sites in the structure [7]. As a result, changes in magnetic ordering at either rare-earth site will affect B_{hf} at both tin sites.

Only the onset of magnetic order can lead to the appearance of a magnetic field at the tin sites, and the fraction of the tin that experiences a magnetic field can be used to eliminate the possibility that the inferred ordering is due to a small concentration of magnetic impurities. ^{119}Sn Mössbauer spectroscopy is both phase specific, as contributions from multiple phases can be distinguished, and phase quantitative, as relative amounts of any phases present can be determined.

We find that $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ fits the expected de Gennes scaling in figure 1 extremely well and that χ_{ac} provides essentially no objective signature of the bulk transition temperature: neither the clear peak at 8 K nor the much weaker and easily suppressed feature centred near 22 K [11] actually reflect bulk ordering in $\text{Gd}_3\text{Ag}_4\text{Sn}_4$. The 8 K feature in χ' is identified as a spin reorientation transition. By contrast, the bulk ordering temperature of $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ is confirmed to be anomalously low.

2. Experimental methods

Both compounds were prepared by arc-melting stoichiometric quantities of the pure elements (Gd and Cu 99.9 wt%, Ag and Sn 99.999 wt%) under Ti-gettered argon. The alloyed buttons were then sealed under vacuum in quartz tubes and annealed for 20 days at 873 K, followed by water quenching ($\text{Gd}_3\text{Ag}_4\text{Sn}_4$), and for 7 days at 1073 K ($\text{Gd}_3\text{Cu}_4\text{Sn}_4$), respectively. Cu $K\alpha$ x-ray diffraction and electron microprobe analysis confirmed that the majority phase in both samples was the orthorhombic $\text{Gd}_3\text{T}_4\text{Sn}_4$ phase, with less than 5% of the ζ -phase $\text{Ag}_{79}\text{Sn}_{21}$ present in the $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ sample. Fitting of the diffraction patterns using GSAS [16]/EXPGUI [17] gave lattice parameters of: ($\text{Gd}_3\text{Ag}_4\text{Sn}_4$) $a = 15.223(4)$ Å, $b = 7.309(2)$ Å and $c = 4.565(1)$ Å, and ($\text{Gd}_3\text{Cu}_4\text{Sn}_4$) $a = 14.743(4)$ Å, $b = 6.939(2)$ Å and $c = 4.4736(11)$ Å, consistent with other isostructural $\text{R}_3\text{Ag}_4\text{Sn}_4$ alloys [2, 5, 11]. Basic magnetic characterization was carried out on a commercial susceptometer/magnetometer equipped with a 9 T magnet and operated down to 1.8 K.

^{119}Sn transmission Mössbauer spectra were collected on a constant acceleration spectrometer using a 0.4 GBq $^{119\text{m}}\text{Sn}$ CaSnO_3 source with the sample in a helium flow cryostat. A 25 μm Pd filter was used to absorb the Sn $K\alpha$ x-rays also emitted by the source. The spectrometer was calibrated using ^{57}Co and $\alpha\text{-Fe}$, with isomer shifts taken relative to a CaSnO_3 reference absorber. Typical linewidths were 0.50(1) mm s^{-1} full width at half maximum (FWHM). Spectra were fitted with a sum of Lorentzian lines using a conventional nonlinear least-squares minimization routine. Line positions and intensities were derived from a full Hamiltonian solution for combined magnetic and quadrupole interactions [18], except where noted.

3. Results and discussion

The ac susceptibility (χ') for $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ (figure 2) exhibits a marked downturn at about 8 K, which has previously been attributed to the onset of AF order [11]. A fit of the

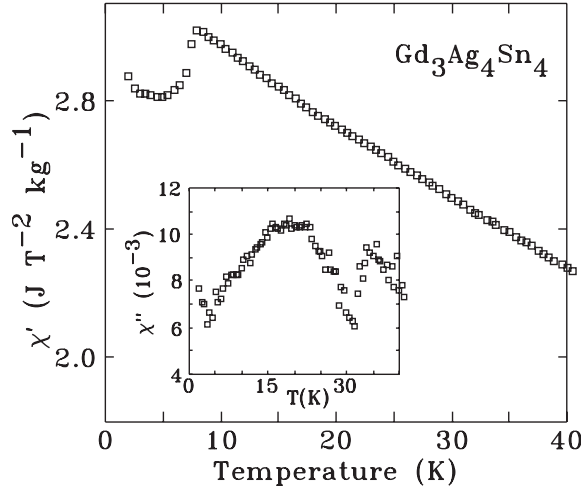


Figure 2. ac susceptibility data (χ') for $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ in a 1 mT ac field at 337 Hz. The inset shows the out-of-phase signal (χ''), which provides the only evidence of the bulk transition near 30 K.

higher-temperature data yields an effective moment (p_{eff}) of $8.16(4) \mu_{\text{B}}$ and a Curie–Weiss temperature (θ_p) of $-50(2)$ K, consistent with the value of -54 K reported previously [11], and reflecting the dominance of antiferromagnetic interactions common to the $\text{R}_3\text{T}_4\text{X}_4$ family of compounds.

No changes in $\chi'(T)$ are apparent other than the feature at 8 K. In particular, we find no direct evidence for the actual onset of long-range magnetic order near 29 K (see below). There is a change in χ'' , the out-of-phase response (shown as an inset to figure 2) near 30 K, however it is difficult to argue that this is a real signature of ordering in $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ as it is clear that we are using knowledge of the actual transition temperature as back justification. In addition, no such feature is seen for $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ below.

Figure 3 shows $\chi'(T)$ for $\text{Gd}_3\text{Cu}_4\text{Sn}_4$. The behaviour is quite similar to that seen for $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ (figure 2), and a fit of $1/\chi'$ versus temperature yields a θ_p of $-59(1)$ K, suggesting slightly stronger AF interactions. The fit also yields a paramagnetic Gd moment of $p_{\text{eff}} = 8.00(4) \mu_{\text{B}}$, close to the free-ion moment of $7.94 \mu_{\text{B}}$. There is a broad feature centred near 8 K with some structure evident at lower temperatures, suggesting an ordering temperature of about 8 K. However, specific heat measurements place the bulk ordering temperature at about 13 K [13], in a region where no marked changes in $\chi'(T)$ are apparent. No significant features could be found in $\chi''(T)$. However, closer examination of the ac-susceptibility data reveals a slight change in slope (emphasized by plotting $d\chi'/dT$ on figure 3) above 12 K.

The temperature derivative of $\chi'(T)$ also shows two marked peaks, at $7.9(1)$ and $6.4(1)$ K, that are consistent with events reported in heat capacity (C_p) data (at 8.2 and 6.5 K) [13]. The entropy of the 8 K event is comparable to that associated with the primary ordering at 13 K, and has been attributed to a magnetic realignment, while the remarkably sharp feature in $C_p(T)$ near 6 K was identified as characteristic of a first-order event.

While the $d\chi'/dT$ features at 8 and 6 K are quite clear, they are not expected to be associated with bulk ordering, which $C_p(T)$ places at about 13 K, where we see only a weak break in slope. As with the $\chi''(T)$ behaviour observed for $\text{Gd}_3\text{Ag}_4\text{Sn}_4$, it is unlikely that the small change in slope would be considered a signature of bulk ordering without prior knowledge of the heat capacity data to bias the search.

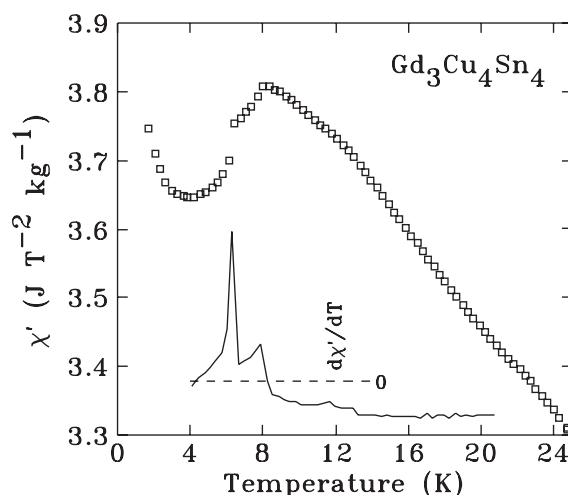


Figure 3. ac susceptibility (χ') for $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ at 337 Hz in a drive field of 1 mT. The temperature derivative ($d\chi'/dT$) is shown as a solid line (see text).

The absence of a clear, objectively identifiable and consistent signature of bulk magnetic ordering in the susceptibility of both $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ and $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ demonstrates the weakness of $\chi'(T)$ data taken in isolation. We turn to ^{119}Sn Mössbauer spectroscopy to obtain an unequivocal picture of the bulk magnetic ordering in these compounds.

3.1. $\text{Gd}_3\text{Ag}_4\text{Sn}_4$

It is immediately clear from the spectra shown in figure 4 that magnetic order is present well above the 8 K ordering temperature inferred from the χ' data shown in figure 2. Visual inspection yields an estimate of 27–30 K, well above any previously suggested value [11]. No significant (<2%) impurity contribution was detected at any temperature, so the behaviour observed here using ^{119}Sn Mössbauer spectroscopy definitely reflects bulk ordering of the primary phase.

Unlike ^{57}Fe , where magnetically split hyperfine patterns are present as six lines with fairly uniform spacing, the Mössbauer pattern for ^{119}Sn in the presence of a magnetic field appears as two triplets. At small fields the triplets may not be fully resolved, especially if the lines are broad, and the observed pattern often resembles a doublet, with each line broadened towards the centre of the spectrum.

Examination of the $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ spectrum at 2.3 K in figure 4 reveals two equal-area magnetic patterns with different hyperfine fields (9.4 and 4.5 T) consistent with the two tin sites in the structure (4f and 4h) and comparable to fields seen in $\text{Sm}_3\text{Ag}_4\text{Sn}_4$ [19], $\text{Tb}_3\text{Ag}_4\text{Sn}_4$ [14] and $\text{Dy}_3\text{Ag}_4\text{Sn}_4$ [6]. Both patterns exhibit significantly broadened lines (FWHM of 1.16(4) mm s^{-1} at 2.3 K compared with 0.55(2) mm s^{-1} at 30 K) and this broadening decreases with increasing temperature as the magnetic splitting is lost. This evolution in linewidth suggests that there is an unresolved distribution of hyperfine fields ($\delta B_{\text{hf}}/B_{\text{hf}} \sim 10\%$) at each of the tin sites resulting from a complex ordering of the gadolinium moments.

As gadolinium is the only magnetic species present in this compound, and the field at the tin sites is transferred from the surrounding Gd moments, we fit the temperature dependence of B_{hf} at each of the two sites with a $J = \frac{7}{2}$ Brillouin function to obtain an average Néel

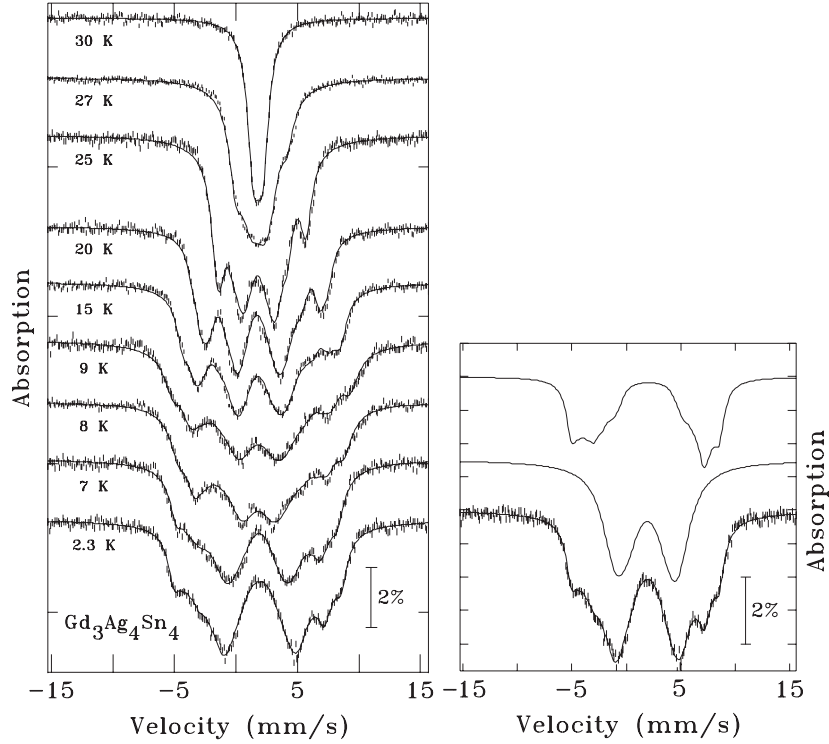


Figure 4. ^{119}Sn Mössbauer spectra of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$. Left-hand panel shows the temperature dependence of the spectra and the onset of magnetic order below ~ 30 K. Solid lines are fits, described in the text. Right-hand panel shows the two equal-area subspectra used to fit the 2.3 K spectrum.

temperature (T_N) of 28.8(2) K for $\text{Gd}_3\text{Ag}_4\text{Sn}_4$. As noted above, there is no clear signature in $\chi'(T)$ (figure 2) associated with this bulk ordering transition. Further examination of $B_{\text{hf}}(T)$ reveals a marked change in the temperature dependence of both components below 9 K, with the high-field component showing an initial decrease and the lower-field component increasing. This behaviour stands in strong contrast with that seen in $\text{Tb}_3\text{Ag}_4\text{Sn}_4$ [14], where both $\chi'(T)$ and neutron diffraction [20] show a second transition at ~ 12 K but only the low- B_{hf} component changed at the second transition. However, the transferred field in $\text{Sm}_3\text{Ag}_4\text{Sn}_4$ [19] also shows changes at both sites below the 8 K transition. In all cases the changes in B_{hf} are about 1 T. The two transitions in $\text{Gd}_3\text{Ag}_4\text{Sn}_4$, $\text{Sm}_3\text{Ag}_4\text{Sn}_4$ and $\text{Tb}_3\text{Ag}_4\text{Sn}_4$ are much better separated in temperature than they are in $\text{Dy}_3\text{Ag}_4\text{Sn}_4$ [6], where only a weak signature of the lower transition could be found in $d\chi'/dT$ (at 14 K, just below the T_N of 16 K) and it fell to neutron diffraction to establish both the existence and nature of the two events [6].

Neutron diffraction is not a realistic option for $\text{Gd}_3\text{Ag}_4\text{Sn}_4$. However, using ^{119}Sn Mössbauer spectroscopy, we are able to establish that the onset of bulk magnetic order occurs at $T_N = 28.8(2)$ K, with a further major reorganization of the spin structure at 8 K. The broad lines and significant overlap present at all temperatures effectively preclude detailed analysis using a full Hamiltonian solution. However, if we assume that a first-order solution is adequate, and treat the electric field gradient (efg) as being axially symmetric, then we can write the observed quadrupole shift Δ as:

$$\Delta = \frac{eQV_{zz}}{4}(3\cos^2\theta - 1) \quad (1)$$

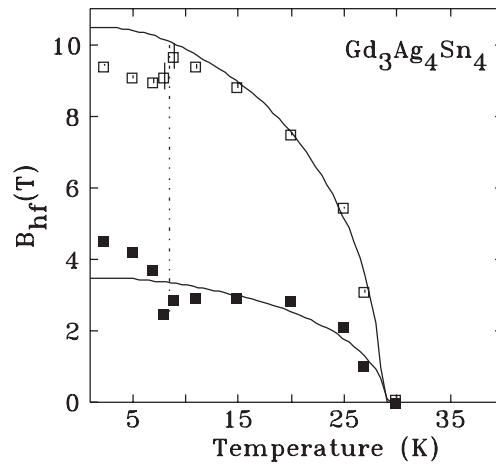


Figure 5. Temperature dependence of the ^{119}Sn hyperfine field (B_{hf}) in $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ showing the onset of bulk magnetic order at 28.8(2) K. There is an additional change below 9 K (dotted line) that marks a reorientation of the Gd moments.

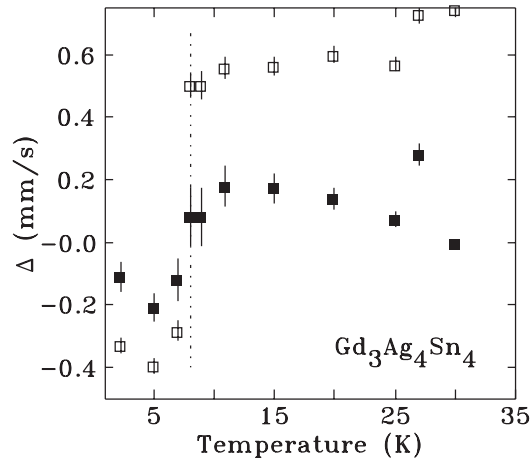


Figure 6. Temperature dependence of quadrupole shift (Δ) in $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ showing the reorientation below 8 K (dotted line). Symbols used correspond to those in figure 5.

where θ is the angle between the z -axis of the efg (determined by the crystallographic environment) and B_{hf} (due to the surrounding magnetic moments). Within this approximation, Δ represents the projection of the efg onto B_{hf} at each of the two tin sites. Plotting the temperature dependence of this projection in figure 6 reveals evidence for a change in field direction below 8 K in addition to the changes in B_{hf} apparent in figure 5. The change in Δ is close to a factor of -2 at both tin sites. This is best seen at the high-field site, where line overlap is less severe and the fits are more reliable: Δ changes from $\sim 0.6 \text{ mm s}^{-1}$ above 8 K to $\sim -0.3 \text{ mm s}^{-1}$ below 8 K. This change suggests that there is a $\sim 90^\circ$ change in the orientation of the hyperfine field at the two tin sites. Our analysis leads us to conclude that the 8 K feature in $\chi'(T)$ that was originally identified as the ordering temperature [11] actually marks a spin reorientation transition.

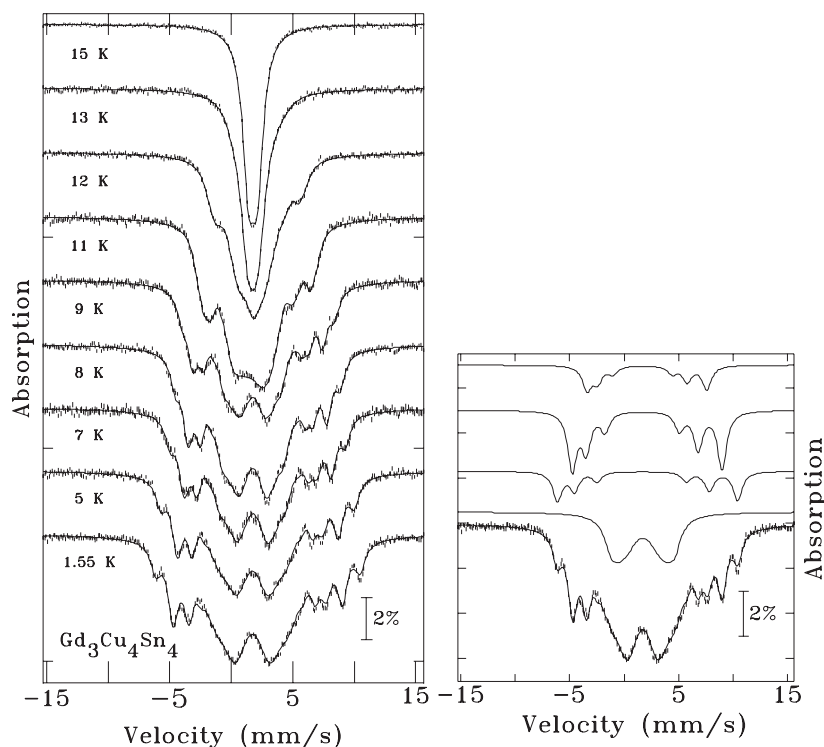


Figure 7. ^{119}Sn Mössbauer spectra of $\text{Gd}_3\text{Cu}_4\text{Sn}_4$. Left-hand panel shows the temperature dependence of the spectra and the onset of magnetic order below ~ 13 K. Solid lines are fits, described in the text. Right-hand panel shows the four components used to fit the 1.55 K spectrum.

3.2. $\text{Gd}_3\text{Cu}_4\text{Sn}_4$

The ^{119}Sn Mössbauer spectrum of $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ at 1.55 K shown in figure 7 is considerably more complex than those of related compounds, with the possible exception of $\text{Dy}_3\text{Ag}_4\text{Sn}_4$ [6]. The characteristic broadened central ‘doublet’ resulting from an unresolved low-field sextet is clearly present and accounts for about half of the total absorption area, as expected for one of the two equipopulous tin sites. However, the pattern of multiple sharp lines at higher velocities (both positive and negative) is far too complex to fit with a single component. We found that a three-component fit with area ratios of 2:1:1 was the minimum set that would account for the observed pattern at high velocities, in addition to the 50% component associated with the low-field pattern. The three high-field components could be traced reliably up to about 11 K before line overlap caused them to blend into each other. We therefore believe that this decomposition of the spectra into a total of four components is correct and that it reflects complex ordering of the gadolinium moments in $\text{Gd}_3\text{Cu}_4\text{Sn}_4$. A similar *three*-component fit to the ^{119}Sn Mössbauer spectra of $\text{Dy}_3\text{Ag}_4\text{Sn}_4$ was found to be consistent with the magnetic structure determined by neutron diffraction [6].

The temperature dependence of all four components is shown in figure 8, where it is clear that they extrapolate to an average Néel temperature of 13.6(1) K, consistent with the ~ 13 K derived from heat capacity data [13]. As with $\text{Gd}_3\text{Ag}_4\text{Sn}_4$, we found no significant impurity contribution in the spectra, and therefore confirm that 13.6(1) K represents the onset of bulk order in $\text{Gd}_3\text{Cu}_4\text{Sn}_4$.

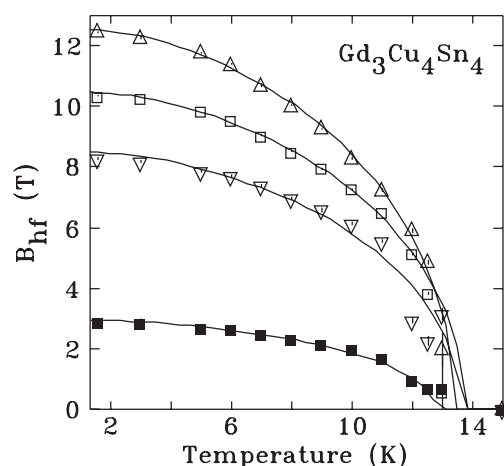


Figure 8. Temperature dependence of the ^{119}Sn hyperfine fields in $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ showing the onset of bulk magnetic order at 13.6(1) K. Solid lines are independent fits to $J = \frac{7}{2}$ Brillouin functions for each component.

Remarkably, we find no evidence for the second, large thermal event at 8.2 K [13] that would correspond with the clear peak seen at 7.9 K in $\chi'(T)$ (figure 3). 8 K is less than $0.6 T_N$ and the fields for all four components are at more than 80% of the saturation values seen at 1.55 K. Magnetic changes are clearly detected in $\text{Tb}_3\text{Ag}_4\text{Sn}_4$ [14], $\text{Sm}_3\text{Ag}_4\text{Sn}_4$ [19] and here in $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ (figure 5), and with the large temperature separation between T_N and the lower event in $\text{Gd}_3\text{Cu}_4\text{Sn}_4$, any major rearrangement of the Gd moments should affect one or more of the tin sites. Indeed, given the extremely complex sub-splitting of the large field component, the potential for detecting changes in the magnetic structure should be greatly enhanced.

Similarly, we see no indication of the first-order event reported to occur at 6.5 K [13]. First-order magnetic transitions have quite clear signatures in the ^{119}Sn Mössbauer spectra of $\text{Tb}_3\text{Ag}_4\text{Sn}_4$ [14] and Gd_5Sn_4 [21], but no changes are detected here in $\text{Gd}_3\text{Cu}_4\text{Sn}_4$, in the subspectral areas, the quadrupole shifts or the hyperfine fields. Again, we feel that the remarkable complexity of the spectra should make it easier to detect major changes in the magnetic structure, especially on the scale implied by $C_p(T)$.

Our $\chi'(T)$ data for $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ are very similar to that reported previously [13], and neither our x-ray data nor our Mössbauer spectra provide any evidence for significant levels of impurities. Finally, the common temperature dependence of the four B_{hf} curves in figure 8 indicates that they all derive from tin atoms in the majority $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ phase. The results obtained here using ^{119}Sn Mössbauer spectroscopy do not support the existence of further spin rearrangements below T_N in $\text{Gd}_3\text{Cu}_4\text{Sn}_4$. The discrepancy between the Mössbauer and $C_p(T)$ data would be best settled using neutron diffraction, however the associated experimental difficulties make it unlikely that the work will be undertaken. While ^{155}Gd Mössbauer spectroscopy might also be considered, the resolution is much poorer and, as we expect that most of the changes are due to reorientations, the effects on the local environment of the Gd atoms are likely to be quite small.

4. Conclusions

Our ^{119}Sn Mössbauer study of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ shows that T_N has been significantly underestimated and that there is essentially no signature of the bulk ordering event in $\chi'(T)$. When the corrected

value (28.8(2) K) is used, the ordering of $\text{Gd}_3\text{Ag}_4\text{Sn}_4$ follows the expected de Gennes scaling for the $\text{R}_3\text{T}_4\text{Sn}_4$ ($\text{T} = \text{Cu}, \text{Ag}$) compound series (figure 1).

By contrast, T_N for $\text{Gd}_3\text{Cu}_4\text{Sn}_4$ is confirmed to be anomalously low at only 13.6(1) K, as reported earlier from $C_p(T)$ data [13]. However, we are unable to provide any confirmation of the events reported at 8.2 or 6.5 K, despite detecting weak signatures of both in $\chi'(T)$.

It is clear that caution is needed when determining transition temperatures from methods that are unable to distinguish the actual source of the signal (e.g. $\chi'(T)$ and $C_p(T)$) and, where possible, corroboration should be sought from other, phase-specific methods (e.g. neutron diffraction or Mössbauer spectroscopy).

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