Complex magnetic ordering in $Tb_3Ag_4Sn_4$

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$Tb_3Ag_4Sn_4$ has been studied using both bulk magnetization and ^{119}Sn Mössbauer spectroscopy. We find evidence for a first-order magnetostructural transition at 28 K, followed by a spin reorientation at 13 K. Three tin sites with hyperfine fields of 8.0, 4.2, and 3.5 T are observed at 2 K with area ratios of 2:1:1. Magnetization at 5 K is linear up to 9 T, indicating antiferromagnetic ordering. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2162826]

I. INTRODUCTION

The orthorhombic $R_3T_4X_4$ family (where R is a rare earth, T=Cu, Ag, Au, and X=Si, Ge, Sn) represents an extensive series of isostructural compounds that exhibit a rich variety of magnetic ordering. They crystallize in an orthorhombic $Gd_3Cu_4Ge_4$-type structure (space group *Immm*, No. 71).[1] The rare-earth atoms occupy two crystallographically distinct sites (4*e* and 2*d*) and their moments order antiferromagnetically (AF), often with quite different moment values[2,3] and with distinct magnetic structures adopted by the two rare-earth sublattices. In some cases the two rare-earth sites will also have two quite different ordering temperatures.[4]

As part of our on-going study of this complex alloy system, we turn to the compound $Tb_3Ag_4Sn_4$. We present here the results of bulk characterization by susceptibility and magnetization, complemented by a microscopic investigation of the ordering using ^{119}Sn Mössbauer spectroscopy. We find two magnetic ordering transitions, with evidence for the upper one being a first-order event, possibly involving a change in crystal structure.

II. EXPERIMENTAL METHODS

A stoichiometric quantity of the pure elements (99.9 wt. % Tb and 99.999 wt. % Ag and Sn) was induction melted in a sealed tantalum crucible under high-purity argon. The alloy button was then sealed under vacuum in quartz tubes and annealed for 20 days at 873 K followed by water quenching. Cu Kα x-ray-diffraction and electron microprobe analyses confirmed that the majority phase was the orthorhombic $Tb_3Ag_4Sn_4$ alloy, with less than 5% of the ζ-phase $Ag_{79}Sn_{21}$. Fitting of the diffraction patterns using GSAS (Ref. 5)/EXPGUI (Ref. 6), gave lattice parameters of a =15.1581(4) Å, b=7.3034(17) Å, and c=4.5502(11) Å, consistent with other isostructural $R_3Ag_4Sn_4$ alloys.[7,8] Basic magnetic characterization was carried out on a commercial susceptometer/magnetometer. ^{119}Sn transmission Mössbauer spectra were collected on a constant acceleration spectrometer using a 0.4 GBq ^{119m}Sn $CaSnO_3$ source with the sample in a helium flow cryostat. The spectrometer was calibrated using ^{57}Co and α-Fe. Spectra were fitted using a conventional nonlinear least-squares minimization routine.

III. RESULTS AND DISCUSSION

The temperature dependence of the ac susceptibility, $\chi_{ac}(T)$, of $Tb_3Ag_4Sn_4$ in a drive field of 1 mT at 137 Hz (Fig. 1) clearly shows evidence of two magnetic transitions at 13 and 28 K. However, $\chi_{ac}(T)$ measured in the presence of a 1 T dc bias field shows only the lower transition at 13 K, the 28 K event being suppressed. Fitting the high-temperature

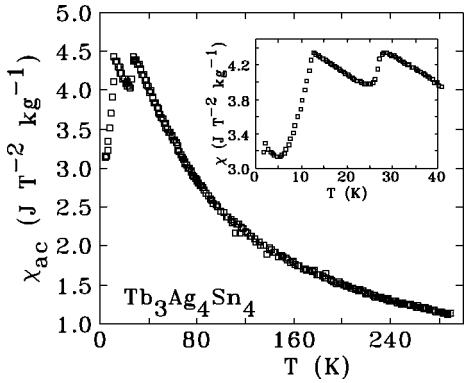

FIG. 1. ac susceptibility (χ_{ac}) as a function of temperature for $Tb_3Ag_4Sn_4$. Inset shows region below 40 K in more detail. Two magnetic transitions at 13 and 28 K are apparent.

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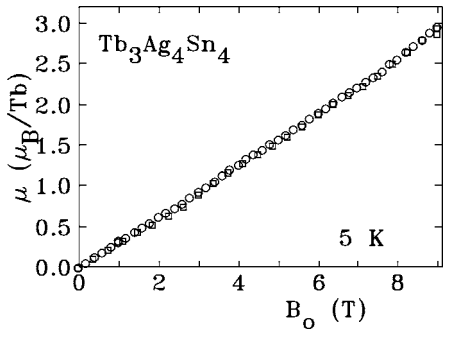

FIG. 2. Magnetization vs field for $Tb_3Ag_4Sn_4$ at 5 K.

region (150–300 K) of $\chi_{ac}(T)$ to a Curie-Weiss law yields $\theta_{CW}=-11$ K, confirming that the dominant exchange interactions are antiferromagnetic. The fit also yields an effective moment of 9.90(5) μ_B/Tb, close to the expected 9.72 μ_B/Tb. The linear field dependence of the magnetization at 5 K (Fig. 2) is consistent with AF ordering of the Tb moments and remains well below saturation in our maximum field of 9 T.

^{119}Sn Mössbauer spectroscopy provides an ideal window onto the magnetic ordering in these complex $R_3T_4Sn_4$ alloys. Tin has no magnetic moment, so that any hyperfine field (B_{hf}) observed in a ^{119}Sn Mössbauer spectrum must be due to ordered moments on neighboring sites. The tin atoms in $R_3T_4Sn_4$ occupy two crystallographic sites (4*f* and 4*h*) and both tin sites have neighbors from each of the two rare-earth sites in the structure.[4] As a result, changes in magnetic ordering at either rare-earth site will affect B_{hf} at both tin sites.

At 45 K, the alloy is paramagnetic and the ^{119}Sn Mössbauer spectrum consists of two unresolved equal-area quadrupole doublets, consistent with the crystal structure. At 2 K, well below both ordering transitions seen in the susceptibility, the spectrum is well split, showing significant hyperfine fields (see Fig. 3). Analysis of this 2 K spectrum, however, reveals a significant contradiction: It does not consist of the two equal-area magnetic sextets demanded by the crystal structure. The more widely split sextet with $B_{hf}=8.00(1)$ T (which we will label Sn_A) does account for half of the total area, but the remaining contribution cannot be fitted with a single sextet without invoking an unrealistic linewidth, and even then a severe misfit is observed. Dividing the second, lower field component further into two equal halves (Sn_{B_1} with $B_{hf}=4.22(3)$ T and Sn_{B_2} with $B_{hf}=3.53(3)$ T) gives a far better fit and also permits a common linewidth to be used for all three components at all temperatures. However, the 2:1:1 area ratio observed in the fit to the 2 K Mössbauer spectrum is not immediately consistent with the constraints imposed by the room-temperature crystal structure.

The temperature dependence of B_{hf} at the Sn_{B_1} and Sn_{B_2} sites clearly shows the effects of the lower transition, T_{N_1}, at 13.5(5) K (Fig. 4). However, essentially no change in B_{hf} is seen at the Sn_A site. We also find that the electric-field gradient (efg) at the Sn_B sites undergoes a marked change at T_{N_1}. Since we are using a first-order perturbation expansion in the fitting, we are sensitive only to the projection of the efg onto the magnetic-field direction through

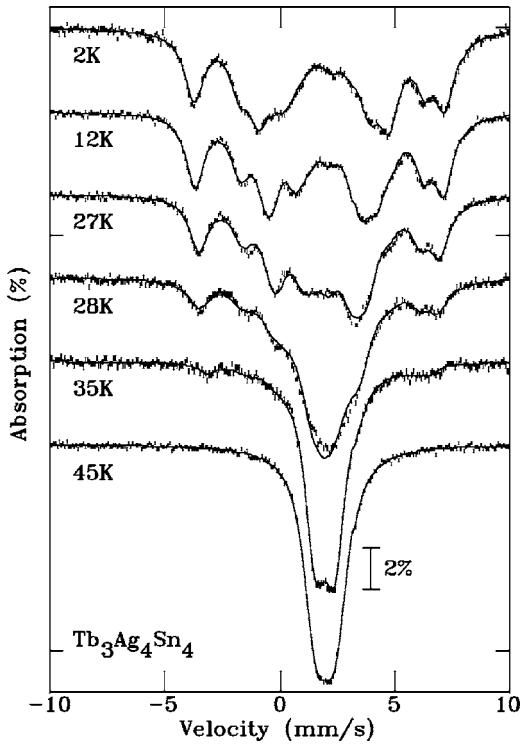

FIG. 3. ^{119}Sn Mössbauer spectra of $Tb_3Ag_4Sn_4$. Solid lines are fits described in the text.

$$\text{efg} \propto V_{zz}(3\cos^2\theta - 1),$$

where V_{zz} is the principal component of the efg tensor and θ is the angle between V_{zz} and B_{hf} (an axially symmetric efg is assumed here). It is unlikely that a crystallographic distortion large enough to cause the observed changes in the efg at the two Sn_B sites would not also affect the Sn_A site; therefore it is more probable that the change occurs in θ, i.e., the angle between V_{zz} and B_{hf}. A change in the orientation of B_{hf} relative to V_{zz} combined with a reduction in the size of B_{hf} could be caused by a loss of magnetic order at one of the two Tb sites, making $Tb_3Ag_4Sn_4$ similar to the $Er_3Cu_4X_4$ system where the two Er sites have quite different ordering temperatures.[2–4] Alternatively, the change could be due to a

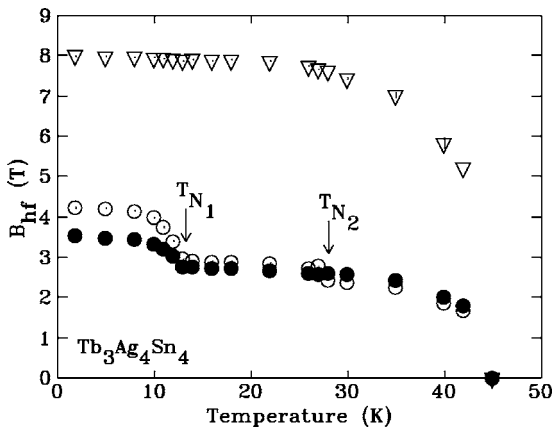

FIG. 4. Temperature dependence of the hyperfine fields (B_{hf}) at the three sites in $Tb_3Ag_4Sn_4$ showing the two magnetic transitions at T_{N_1} and T_{N_2}. ○ and ● show the fields for the Sn_{B_1} and Sn_{B_2} sites (areas=1:1), while ▽ shows B_{hf} at the Sn_A site (area=2). See text for details.

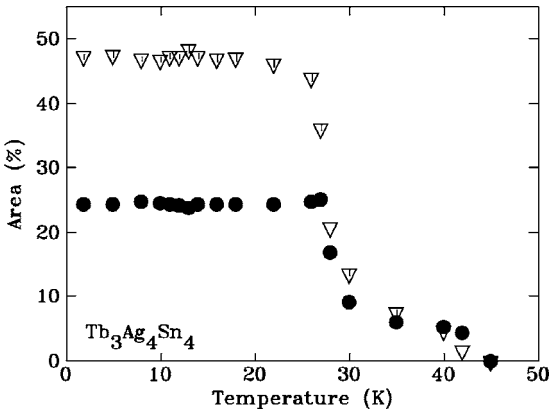

FIG. 5. Temperature dependence of the areas of the three components in the ^{119}Sn Mössbauer spectra of $Tb_3Ag_4Sn_4$ showing a transition at ~28 K. ○ and ● show the Sn_{B_1} and Sn_{B_2} sites, while ▽ shows the Sn_A site.

rotation of the magnetic ordering direction at one of the two Tb sites (a change at both Tb sites would almost certainly affect the high-field site as well, as both crystallographic tin sites have first-neighbor terbium atoms from both crystallographic Tb sites), making T_{N_1} a spin reorientation transition rather than a distinct ordering temperature. The ^{119}Sn Mössbauer data do not permit us to distinguish these two cases without additional information.

χ_{ac} in Fig. 1 clearly places the second transition at 28 K, but it is equally clear from Fig. 4 that little, if anything, happens in $B_{hf}(T)$ at any of the tin sites. Indeed, extrapolation of $B_{hf}(T)$ for all three tin sites leads to a common transition temperature of 44(1) K, where $\chi_{ac}(T)$ is essentially featureless. Closer examination of the spectra in Fig. 3 shows that $B_{hf}(T)$ does not tell the whole story. The line near −4 mm/s is a prominent feature of the 2 K spectrum and is the leftmost line of the sextet due to the Sn_A site. With increasing temperature, this line moves to a slightly more positive velocity as B_{hf} falls; however, it also decreases markedly in intensity (compare the 28 and 35 K spectra in Fig. 3). Similar behavior is also observed at the Sn_{B_1} and Sn_{B_2} sites, although their splittings are much smaller and the changes are largely masked by the growth of the central paramagnetic components. The fitted area changes are shown in Fig. 5 and this confirms that it is the collapse of the *area* of the magnetic components that corresponds to T_{N_2} in χ_{ac} and not the collapse of the field as would be expected for a second-order magnetic transition.

The temperature dependences of B_{hf} (Fig. 4) and spectral areas (Fig. 5) are precisely those that would be expected for a first-order magnetostructural transition as is seen in the R_5X_4 giant magnetocaloric materials.[9,10] The bulk of the transformation occurs between 24 and 30 K and it would appear that the upper feature in $\chi(T)$ (Fig. 1) seen at ~28 K corresponds to the steepest decline in magnetic area in Fig. 5 at 27.5(5) K. Remarkably, enough of the low-temperature phase persists at temperatures above which most of the material has transformed into the high-temperature form, and this allows us to estimate an ordering temperature of 44(1) K for the low-temperature form. However, we see no indications of magnetic order in the high-temperature form as it transforms before any magnetic order can develop.

Our measurements suggest that $Tb_3Ag_4Sn_4$ undergoes a first-order magnetostructural transition at 28 K, followed by a spin reorientation at 13 K. A change in crystal structure at 28 K is also consistent with the observed 2:1:1 area ratios for the $Sn_A:Sn_{B_1}:Sn_{B_2}$ sites in the 2 K ^{119}Sn Mössbauer spectrum. A neutron-diffraction study is underway to investigate this system in more detail.

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[1] W. Rieger, Monatsch. Chem. **101**, 449 (1970).
[2] E. Wawrzyńska, J. Hernandez-Velasco, B. Penc, W. Sikora, A. Szytuła, and A. Zygmunt, J. Phys.: Condens. Matter **15**, 5279 (2003).
[3] E. Wawrzyńska, J. Hernandez-Velasco, B. Penc, A. Szytuła, and A. Zygmunt, J. Magn. Magn. Mater. **264**, 192 (2003).
[4] D. H. Ryan, J. M. Cadogan, R. Gagnon, and I. P. Swainson, J. Phys.: Condens. Matter **16**, 3183 (2004).
[5] A. C. Larson and R. B. Von Dreele, "General Structure Analysis System (GSAS)," Los Alamos National Laboratory Report No. LAUR 86-748, 2000; www.ncnr.nist.gov/programs/crystallography/software/gsas.html
[6] B. H. Toby, J. Appl. Crystallogr. **34**, 210 (2001).
[7] E. Wawrzyńska, J. Hernandez-Velasco, B. Penc, A. Szytuła, and K. Tomala, J. Phys.: Condens. Matter **16**, 7535 (2004).
[8] D. Mazzone, P. Riani, M. Napoletano, and F. Canepa, J. Alloys Compd. **387**, 15 (2005).
[9] K. A. Gschneidner, V. K. Pecharsky, A. O. Pecharsky, V. V. Ivtchenko, and E. M. Levin, J. Alloys Compd. **303–304**, 214 (2000).
[10] D. H. Ryan, M. Elouneg-Jamróz, J. van Lierop, Z. Altounian, and H. B. Wang, Phys. Rev. Lett. **90**, 117202 (2003).