JOURNAL OF APPLIED PHYSICS **105**, 07D508 (2009)

^{119}Sn Mössbauer spectroscopy investigation of $Nd_3Cu_4Sn_4$, $Nd_3Ag_4Sn_4$, and $Ho_3Cu_4Sn_4$

C. J. Voyer,[1,a)] D. H. Ryan,[1] and J. M. Cadogan[2]
[1]*Centre for the Physics of Materials and Department of Physics, McGill University, Montréal, Quebec H3A 2T8, Canada*
[2]*Department of Physics and Astronomy, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

(Presented 12 November 2008; received 15 September 2008; accepted 29 October 2008; published online 9 February 2009)

$Nd_3Cu_4Sn_4$, $Nd_3Ag_4Sn_4$, and $Ho_3Cu_4Sn_4$ have been studied using ^{119}Sn Mössbauer spectroscopy. Contrary to recent neutron diffraction data, $Nd_3Cu_4Sn_4$ shows a clear magnetic signal at 1.6 K and has an ordering temperature of 2.0(1) K. $Nd_3Ag_4Sn_4$ orders at 4.8(1) K, in agreement with neutron diffraction measurements. We observe the ordering of the Ho 2*d* sublattice in $Ho_3Cu_4Sn_4$ at 8.2(1) K but we also see some residual magnetic splitting up to 10.5(2) K, which was not previously detected by neutron scattering. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3063072]

I. INTRODUCTION

The ternary rare-earth series of compounds $R_3T_4Sn_4$ (T=Cu, Ag) adopts the orthorhombic $Gd_3Cu_4Ge_4$-type structure (space group *Immm*, No. 71).[1] The rare-earth atoms occupy two crystallographically distinct sites (2*d* and 4*e*), the transition metal (T) occupies the 8*n* site, and the Sn atoms fill the 4*f* and 4*h* sites. Some exhibit simultaneous order of both R sublattices,[2–4] while others have separate ordering temperatures for each R sublattice.[4–6] In many cases there are additional changes in the magnetic structure on further cooling[2,4,5,7] and one example of a coupled first-order magnetostructural transition has been reported.[8]

One remarkable feature is that bulk measurements (e.g., magnetic susceptibility and magnetization) frequently miss the primary ordering event and have led to severe underestimates of T_N in, for example, $Gd_3Ag_4Sn_4$ (Ref. 7) and $Sm_3Ag_4Sn_4$.[9] ^{119}Sn Mössbauer spectroscopy is a local probe of the magnetism, does not require long range order, and can detect weak magnetism more easily than other conventional techniques. In this paper we present ^{119}Sn Mössbauer spectroscopy results from $Nd_3Cu_4Sn_4$, $Nd_3Ag_4Sn_4$, and $Ho_3Cu_4Sn_4$. This work is part of a project aimed at collecting systematic data on the $R_3T_4Sn_4$ series in order to develop a more complete understanding of the delicate balance of factors that control their magnetic ordering.

II. EXPERIMENTAL METHODS

Samples were prepared in a triarc furnace with a base pressure of better than 6×10^{-7} mbar. Stoichiometric amounts of pure elements (99.9 wt % Ho, Nd, and Cu and 99.999 wt % Ag and Sn), with an excess of 10 wt % Ag which compensated for losses due to the high vapor pressure of Ag, were melted several times under pure (<1 ppm impurity) argon to ensure homogeneity. The ingots were sealed in quartz tubes with a partial pressure of He, annealed at 800 °C for 1 week, and water quenched. Cu K_α x-ray diffraction patterns were fitted with GSAS (Ref. 10) via the EXPGUI (Ref. 11) user interface and confirmed sample purity ($Nd_3Cu_4Sn_4$ with <5 wt % $NdCu_2Sn_2$, $Nd_3Ag_4Sn_4$ with <2 wt % NdAgSn, and $Ho_3Cu_4Sn_4$ with no detected impurity). Lattice parameters are listed in Table I. Several attempts were made to obtain a $Ho_3Ag_4Sn_4$ sample; however, the result was always a mixture of HoAgSn and $HoAgSn_2$.

^{119}Sn Mössbauer spectra were collected using standard methods[7] and fitted using a conventional nonlinear least-squares minimization routine with an exact solution to the full Hamiltonian with combined magnetic dipole and electric quadrupole interactions.[12]

The Sn 4*h* site has two rare-earth 2*d* neighbors (R 2*d*) and four equidistant R 4*e* neighbors, while the Sn 4*f* site has one R 2*d* neighbor and four R 4*e* neighbors (in two sets of equidistant pairs, one approximately 0.5 Å further than the other depending on the lattice parameters). The transferred hyperfine field B_{hf} observed at the Sn 4*f* and Sn 4*h* sites should therefore be sensitive to magnetic ordering on both rare-earth sites, and we expect at least two magnetic components in the ^{119}Sn Mössbauer spectra. The diverse magnetic

TABLE I. Room temperature lattice parameters, quadrupole splittings Δ in the paramagnetic state, and the transferred hyperfine magnetic fields B_{hf} at each site obtained at 1.6 K.

Compound	Lattice parameters (Å)	Δ (mm/s)	B_{hf} (T)
$Nd_3Cu_4Sn_4$	a=14.951(2)		1.95(2)
	b=6.984(1)	0.837(4)	1.12(2)
	c=4.544(1)		
$Nd_3Ag_4Sn_4$	a=15.389(4)		5.43(2)
	b=7.332(2)	0.783(5)	1.32(2)
	c=4.630(1)		
$Ho_3Cu_4Sn_4$	a=14.578(3)		3.89(1)
	b=6.907(1)	0.78(1)	1.79(2)
	c=4.420(1)		

[a)]Electronic mail: voyerc@physics.mcgill.ca.

0021-8979/2009/105(7)/07D508/3/$25.00

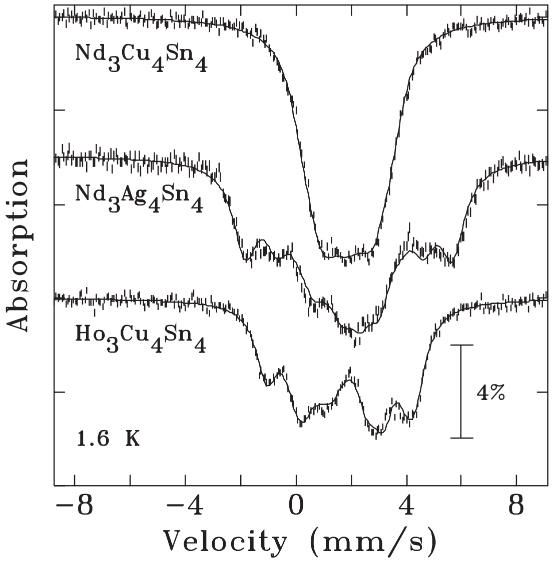

FIG. 1. 1.6 K ^{119}Sn Mössbauer spectra for $Nd_3Cu_4Sn_4$ (top), $Nd_3Ag_4Sn_4$ (middle), and $Ho_3Cu_4Sn_4$ (bottom). All three samples clearly exhibit splitting due to the presence of a transferred magnetic field at the two Sn sites in the structure.

structures adopted by these compounds have led to the observation of a variety of different magnetic ^{119}Sn Mössbauer spectra, with saturated fields that vary from 12.5 T (Ref. 3) to 3 T (Ref. 6) for the high field component and from 3.7 T (Ref. 7) to 1 T (Ref. 6) for the low field component.

III. RESULTS AND DISCUSSION

A. $Nd_3Cu_4Sn_4$ and $Nd_3Ag_4Sn_4$

Neutron diffraction showed no magnetic signal at 1.5 K (Ref. 13) for $Nd_3Cu_4Sn_4$ even though the transition temperature inferred from magnetic susceptibility and heat capacity[14] is just below 2 K. We clearly see a magnetic splitting in the ^{119}Sn Mössbauer spectrum acquired at 1.6 K (Fig. 1) and observe two equal-area subspectra, consistent with the equal populations of the two inequivalent Sn sites in the crystal structure, one with a field of 1.95(2) T and the other with a field of 1.12(2) T.

Fitting a Brillouin function (with $J=\frac{9}{2}$, the value for Nd^{3+}) to the temperature dependence of each component yields an average transition temperature of 2.0(1) K and extrapolated 0 K fields of 2.9(1) and 1.9(3) T, indicating that the fields at 1.5 K are $\sim 2/3$ of their saturation value. Our preliminary neutron diffraction results on this sample at 0.38 K show a clear magnetic contribution, suggesting that a magnetic signal should be visible at 1.5 K.

The ^{119}Sn Mössbauer spectrum of $Nd_3Ag_4Sn_4$ at 1.6 K (Fig. 1) can be fitted with two equal-area components with fields of 5.43(2) and 1.32(2) T. The difference in saturation fields between these two Nd compounds highlights the significant impact that the substitution of Cu for Ag has on the magnetic structure, as found in the Gd case, for example.[7] The temperature dependence of the transferred hyperfine field in $Nd_3Ag_4Sn_4$ (Fig. 2) was fitted with $J=\frac{9}{2}$ Brillouin functions and yielded an average transition temperature of 4.8(1) K, in agreement with the 5 K value obtained by neutron diffraction.[2]

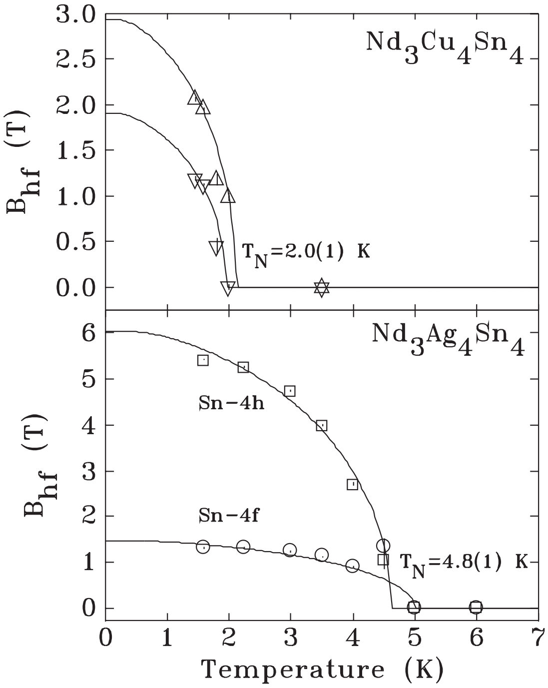

FIG. 2. Temperature dependence of the transferred hyperfine fields in $Nd_3Cu_4Sn_4$ (top) and $Nd_3Ag_4Sn_4$ (bottom), each fitted with $J=\frac{9}{2}$ Brillouin functions. The site assignments for $Nd_3Ag_4Sn_4$ are discussed in the text.

The sharp spectral lines and two equal-area components suggest that both $Nd_3Cu_4Sn_4$ and $Nd_3Ag_4Sn_4$ adopt relatively simple commensurate magnetic structures below T_N. Furthermore, the approximately 2:1 field ratio seen in $Nd_3Cu_4Sn_4$ is similar to that seen in $Ho_3Cu_4Sn_4$ and may indicate that it adopts a magnetic structure in which the Nd 4*e* contributions to the transferred field cancel at both Sn sites (see below).

As both the Nd moments and magnetic structure of $Nd_3Ag_4Sn_4$ are known,[2] we can use them to estimate the transferred fields. The Sn 4*h* site has two Nd 2*d* ($1.3\mu_B$) neighbors oriented parallel to the *a* axis and four Nd 4*e* ($2.3\mu_B$) neighbors aligned in the *ab* plane, making an angle of 144° with the *a* axis. However, the four Nd 4*e* neighbors of the Sn 4*f* site occur as two antiparallel pairs and their contribution is expected to cancel, leaving only a single Nd 2*d* moment to affect the Sn 4*f* site. If we assume that the local field is simply a vector sum over the magnetic neighbors (including the different magnitudes of Nd moments) then we estimate a Sn 4*h*:Sn 4*f* field ratio of 5.6:1 which compares well with the observed ratio of 4.11(6):1 and allows us to assign the higher field component to tin atoms in the Sn 4*h* site.

B. $Ho_3Cu_4Sn_4$

The magnetic behavior of $Ho_3Cu_4Sn_4$ measured by neutron diffraction, heat capacity, and magnetization is quite complex.[15] Neutron diffraction shows that the Ho 2*d* sublattice orders at 7.6 K in an incommensurate structure, then locks in and reorients at 5.5 and 4.4 K, respectively. The Ho 4*e* sublattice orders independently at 3.3 K in an incommen-

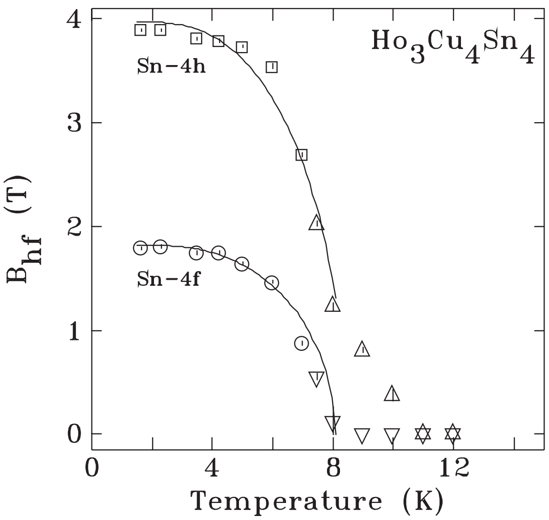

FIG. 3. Temperature dependence of the transferred hyperfine magnetic fields in $Ho_3Cu_4Sn_4$. The solid lines are $J=\frac{1}{2}$ Brillouin function fits to the points below 8 K. The Sn 4*h* (□) and Sn 4*f* (○) site assignments are only considered valid below ~6 K (see text).

surate magnetic structure and undergoes a further reorientation at 2.3 K. Magnetization, however, places the primary ordering temperature at just *above* 8 K.

While the spectrum at 1.6 K (bottom of Fig. 1), shows the expected two-site form, with hyperfine fields of 3.89(1) and 1.79(2) T, the temperature dependence of these fields (Fig. 3) is not simple. We found that $J=\frac{1}{2}$ Brillouin functions (rather than the expected $J=8$) gave the best fits to the basic trends up to 8 K and yielded an average ordering temperature of 8.2(1) K, consistent with magnetization data but somewhat above that inferred from heat capacity. We observe a slight break around 6 K that might be associated with a reorientation of the Ho 2*d* sublattice. A residual transferred field persists up to just above 10 K, suggesting the possible presence of short range magnetic order in the Ho 2*d* sublattice above the primary ordering temperature, similar to what was observed for the Ho 4*e* lattice above its ordering temperature.[15]

Examination of the complex magnetic structure adopted by the Ho 4*e* moments leads us to expect that their contribution to the transferred hyperfine field at *both* tin sites will be zero. The two Ho 2*d* neighbors of the Sn 4*h* site are parallel to each other, and the Sn 4*f* site has a single Ho 2*d* neighbor, leading to a simple prediction of a 2:1 field ratio for Sn 4*h*:Sn 4*f*. The observed ratio at 1.6 K is 2.17(3):1, and this allows us to assign the higher field component to the Sn 4*h* site.

In conclusion, we have confirmed the magnetic ordering of $Nd_3Cu_4Sn_4$ at 2.0(1) K and $Nd_3Ag_4Sn_4$ at 4.8(1) K, although the former result is currently inconsistent with a recent neutron diffraction study. ^{119}Sn Mössbauer spectroscopy confirms that $Ho_3Cu_4Sn_4$ orders at 8.2(1) K, and that a transferred hyperfine field that persists to 10.5(2) K could be due to short range correlations within the Ho 2*d* sublattice. The observed field ratios for the two tin sites in $Nd_3Ag_4Sn_4$ and $Ho_3Cu_4Sn_4$ at 1.6 K are fully consistent with the neutron diffraction derived magnetic structures and permit an unambiguous assignment of the Sn 4*h* (high field) and Sn 4*f* (low field) components in both compounds.

ACKNOWLEDGMENTS

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and Fonds québécois de la recherche sur la Nature et les technologies. J.M.C. is supported by the Canada Research Chairs program.

[1] W. Rieger, Monatsch. Chem. **101**, 449 (1970).
[2] E. Wawrzyńska, J. Hernandez-Velasco, B. Penc, B. Szytula, and K. Tomala, J. Phys.: Condens. Matter **16**, 7535 (2004).
[3] L. K. Perry, J. M. Cadogan, D. H. Ryan, F. Canepa, M. Napoletano, D. Mazzone, and P. Riani, J. Phys.: Condens. Matter **18**, 5783 (2006).
[4] E. Wawrzyńska, J. Hernandez-Velasco, B. Penc, W. Sikora, A. Szytula, and A. Zygmunt, J. Phys.: Condens. Matter **15**, 5279 (2003).
[5] A. Szytuła *et al.*, J. Alloys Compd. **367**, 224 (2004).
[6] D. H. Ryan, J. M. Cadogan, R. Gagnon, and I. P. Swainson, J. Phys.: Condens. Matter **16**, 3183 (2004).
[7] C. J. Voyer, D. H. Ryan, M. Napoletano, and P. Riani, J. Phys.: Condens. Matter **19**, 156209 (2007).
[8] L. K. Perry, D. H. Ryan, F. Canepa, M. Napoletano, D. Mazzone, P. Riani, and J. M. Cadogan, J. Appl. Phys. **99**, 08J502 (2006).
[9] C. J. Voyer, D. H. Ryan, J. M. Cadogan, L. M. D. Cranswick, M. Napoletano, P. Riani, and F. Canepa, J. Phys.: Condens. Matter **19**, 436205 (2007).
[10] A. C. Larson and R. B. von Dreele, Los Alamos National Laboratory Technical Report No. LAUR86-748, 2004.
[11] B. H. Toby, J. Appl. Crystallogr. **34**, 210 (2001).
[12] C. J. Voyer and D. H. Ryan, Hyperfine Interact. **170**, 91 (2006).
[13] E. Wawrzyńska, J. Hernández-Velasco, B. Penc, and A. Szytuła, J. Phys.: Condens. Matter **16**, 45 (2004).
[14] S. Singh, S. K. Dhar, P. Manfrinetti, and A. Palenzona, J. Magn. Magn. Mater. **250**, 190 (2002).
[15] L. Gondek, A. Szytula, D. Kaczorowski, A. Szewczyk, M. Gutowska, and O. Prokhnenko, Intermetallics **15**, 583 (2007).