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Puzzling Magnetism of $Gd_3Cu_4Sn_4$

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A polycrystalline, single phase sample of $Gd_3Cu_4Sn_4$ ($Gd_3Cu_4Ge_4$ type, $Immm$, $a = 1473.5(1)$, $b = 694.1(1)$, $c = 447.2(1)$ pm) was synthesized by arc-melting of the elements and subsequent annealing of the sample at 1220 and 970 K, respectively. The magnetic properties of this compound were studied thoroughly by AC and DC magnetic susceptibility measurements and ^{155}Gd Mössbauer spectroscopy. These results reveal two antiferromagnetic phase transitions close to 13 and 8.6 K, respectively. The thermal variation of the magnetic hyperfine fields observed at two inequivalent Gd sites point to two magnetic substructures, which order independently.

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1. Introduction

$Gd_3Cu_4Sn_4$ crystallizes in the orthorhombic $Gd_3Cu_4Ge_4$-type structure (space group $Immm$) [1] with two symmetry inequivalent Gd sites $2d$ (mmm) and $4e$ (mm) in the unit cell and the nominal occupational ratio 1:2. A puzzling feature for this compound is only one distinct but broad maximum at about 8.4 K revealed by magnetic susceptibility measurements and interpreted as indicating an antiferromagnetic transition while the transition detected by heat capacity $C_p(T)$ at 13 K has only minor influence on the susceptibility data [2]. Recent ^{119}Sn Mössbauer spectroscopy measurements [3] show undoubtedly that this last transition has a magnetic character but no evidence of further spin rearrangements was found below $T_N = 13$ K: i.e. at the 8 K event as well as at another additional 6.5 K transition also revealed by heat capacity experiment [2].

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The aim of the present work was to get a deeper insight into the magnetic nature of $Gd_3Cu_4Sn_4$ using magnetic and ^{155}Gd Mössbauer spectroscopy measurements.

2. Experimental

Starting materials for the preparation of the $Gd_3Cu_4Sn_4$ sample were a gadolinium ingot (Johnson Matthey), copper wire (Johnson Matthey, Ø 1 mm), and tin granules (Merck), all with stated purities better than 99.9%. The polycrystalline sample was obtained using a standard arc-melting procedure, similar to the one described previously [1] and subsequent annealing of the sample at 1220 (7 d) and 970 K (7 d), respectively. $Gd_3Cu_4Sn_4$ was characterized through a powder diffractogram (Stoe StadiP) using Cu K_{α_1} radiation and silicon ($a = 543.07$ pm) as an external standard.

Bulk magnetic measurements were carried out using a Lake Shore 7225 AC susceptometer/DC magnetometer.

^{155}Gd Mössbauer spectra were collected in a transmission geometry cryostat and a conventional Mössbauer spectrometer of an electromechanical type was used in the constant-acceleration mode. The 20 mCi ^{155}Eu:$SmPd_3$ source (86.5 keV, $I_g = 3/2$, E1, $I_e = 5/2$ transition) was kept at 4.2 K to increase the efficiency of the resonance emission. The temperature of the absorber was varied within 4.2 and 20 K, respectively, with a stabilization better than 0.05 K. The absorber was made of the powdered material placed in a thin-walled (0.1 mm) aluminum disk container to ensure a significant transmission for gamma rays and a homogeneous temperature over the whole sample. The absorber was made of the fine powdered compound with an optimized thickness. The resonance 86.5 keV gamma rays were detected by a scintillation NaI(Tl) counter (3 cm thick). A 0.9 mm thick Pb foil was applied as critical absorber to reduce the influence of higher 105.3 keV gamma-ray transition. The drive velocity calibration was performed with a ^{57}Co(Rh) source against a standard metallic iron foil at room temperature. Owing to the low symmetry of the Gd positions, the analysis of the experimental resonance line shapes was carried out by means of least-squares fits using the transmission integral formula with a numerical diagonalization routine of the full hyperfine Hamiltonian [4]. In the case of the ^{155}Gd resonance, the sign of the quadrupole interaction constant E_Q in the ground state and the magnitude of the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ cannot be unambiguously determined in the paramagnetic state because of the small magnitude of the excited state quadrupole moment [5]. Therefore, the absolute value of the effective quadrupole splitting parameter $|\Delta E_Q^{\mathrm{eff}}| = |eQV_{zz}|(1 + \eta^2/3)^{1/2}$ was used to fit the data above T_N.

3. Results and discussion

X-ray analysis of our polycrystalline sample showed that its structure and lattice parameters are in good agreement with those previously determined [1, 2].

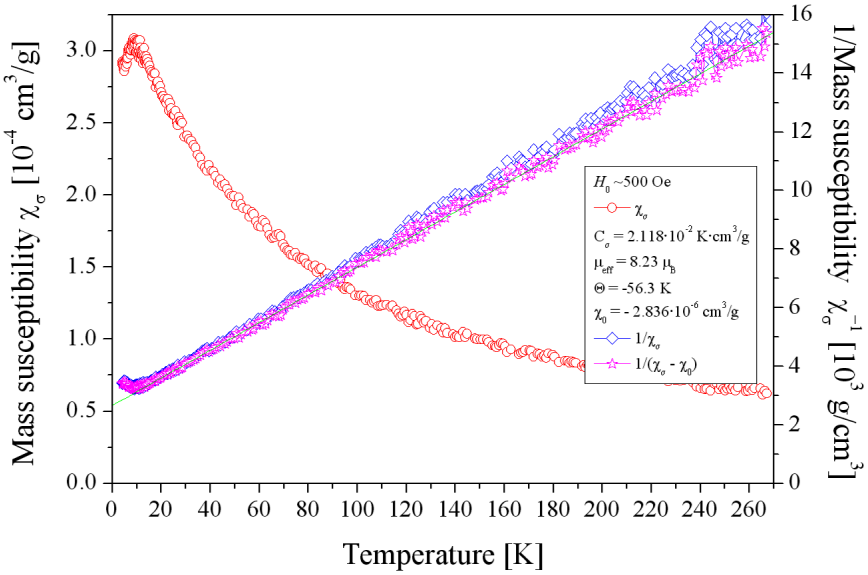

Fig. 1. Temperature dependences of magnetic susceptibility (left-hand scale) and inverse susceptibility (right-hand scale) for $Gd_3Cu_4Sn_4$ in an external magnetic field $H = 500$ Oe.

Above 13 K, the recorded susceptibility (Fig. 1) obeys fairly well a modified Curie–Weiss law in the form $\chi_\sigma = \chi_0 + C/(T - \Theta_p)$, with the temperature independent factor $\chi_0 = -2.8 \times 10^{-6}$ cm^3/g, the Curie constant $C = 2.118 \times 10^{-2}$ K cm^3/g, and the paramagnetic Curie temperature $\Theta_p = -56.2$ K. The relatively big negative paramagnetic Curie temperature indicates a dominant antiferromagnetic exchange interaction among the gadolinium atoms. The effective number p_{eff} of the Bohr magnetons (μ_B) per formula unit was derived from the formula $p_{eff} = (3k_B/N_A)^{1/2}(MC)^{1/2}/\mu_B$ where k_B is the Boltzmann constant, N_A is the Avogadro number, and M is the molar mass expressed in grams. The experimental value of the effective magnetic $\mu_{eff} = 8.23$ μ_B per one Gd ion, calculated from p_{eff}, is slightly higher than the theoretical free-ion value $\mu_{eff} = g\mu_B[J(J+1)]^{1/2} = 7.94$ μ_B for the free Gd^{3+} ion. The AC zero field magnetic susceptibility $\chi'(T)$ data (Fig. 2) show only one broad peak centered at about 8.6 K and a small change of its slope below 13 K. Almost linear behavior of the magnetization curves versus the external magnetic field obtained below 13 K (Fig. 3) confirms the antiferromagnetic character of our sample.

The Mössbauer spectra obtained above and below the magnetic transition temperature are displayed in Fig. 4. As expected for the non-cubic point symmetry of the Gd sites in $Gd_3Cu_4Sn_4$, the Mössbauer spectra show the presence of electric field gradients (EFG) interacting with the ^{155}Gd-nuclei quadrupole moment. In accordance with two crystallographically inequivalent positions in $Gd_3Cu_4Sn_4$, the

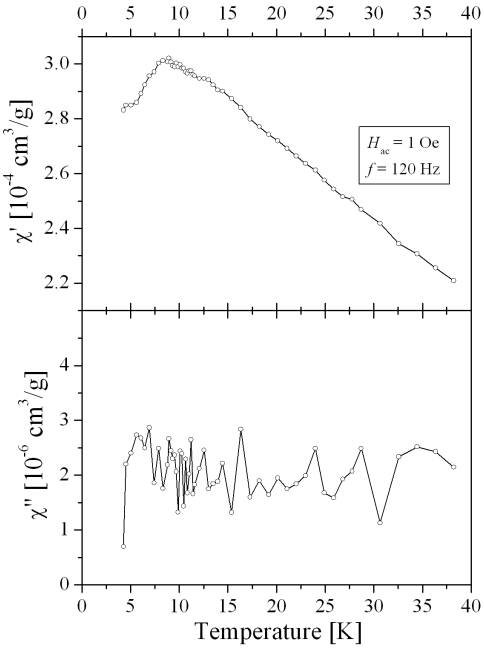

Fig. 2. $Gd_3Cu_4Sn_4$ zero-field susceptibilities χ' and χ'' recorded simultaneously as a function of temperature with an amplitude of the oscillating field $H_{ac} = 1$ Oe at the internal frequency $f = 120$ Hz.

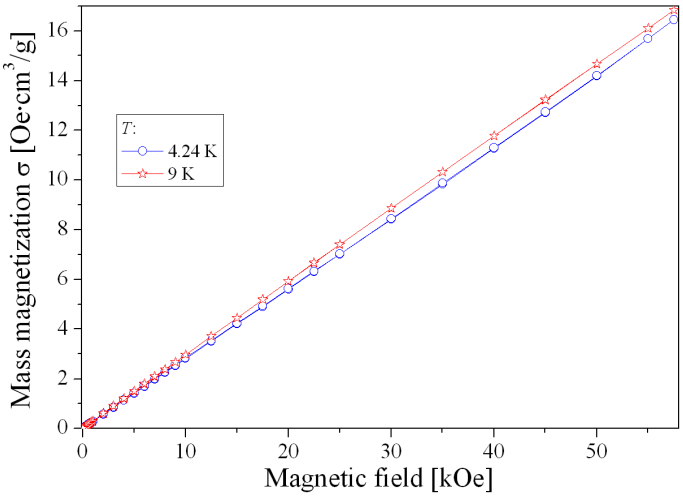

Fig. 3. Mass magnetizations $\sigma(H)$ measured for $Gd_3Cu_4Sn_4$ at 4.24 and 9 K, respectively. The measurements were always started after zero-field cooling of the sample.

spectrum recorded at $T = 20$ K (i.e. above the Néel temperature $T_N = 13(1)$ K in the paramagnetic state, Fig. 4; the top spectrum) can only be fitted with two

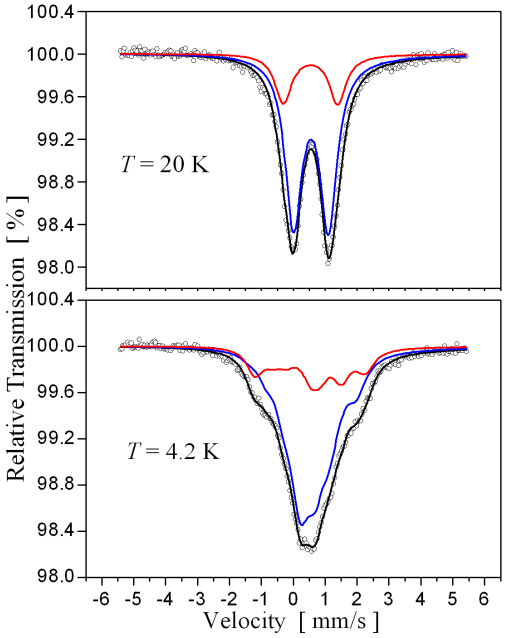

Fig. 4. ^{155}Gd resonance spectra for $Gd_3Cu_4Sn_4$ recorded at $T = 20$ K i.e. in the paramagnetic region (at the top), and at $T = 4.2$ K (at the bottom). The continuous line represents the least-squares fits to the experimental points.

quadrupole split subspectra and the results obtained for both components are presented in Table. Since for different trial fits, the fitted values of the absorber line widths Γ_A had an unphysical tendency to be reduced in comparison to the natural line width $\Gamma = 0.25$ mm/s [5], therefore they were constraint to that result. The value of the obtained effective quadrupole interaction constants $|\Delta E_Q^{eff}|$ can serve for an estimation of a very important solid-state property i.e. the EFG V_{zz} at the gadolinium nuclei, which is related by the simple expression: $V_{zz} = 2.220646 \times 10^{21} \Delta E_Q^{eff}([\text{mm/s}])$ V/m^2. This leads to the values: $|V_{zz}^1| = 5.11 \times 10^{21}$ V/m^2 and $|V_{zz}^2| = 7.96 \times 10^{21}$ V/m^2.

In contrast to the ^{119}Sn Mössbauer spectroscopic investigations, the ^{155}Gd ones are able to follow directly the temperature evolution of the magnetic hyperfine field at both individual Gd sites. The interatomic distances between the Gd atoms in the $2d$ and $4e$ sites are relatively large (≈ 4 Å) suggesting that the coupling between the Gd moments at these two sites are weak and therefore one can expect independent ordering of the two magnetic Gd substructures. As a matter of fact, the ^{155}Gd Mössbauer spectra obtained below T_N can be effectively fitted by only two magnetic subspectra.

Generally, the proper analysis of the magnetically split ^{155}Gd Mössbauer spectra requires the exact knowledge on the relation between the local symmetry

TABLE

Hyperfine interaction parameters inferred from the ^{155}Gd resonance spectra obtained for $Gd_3Cu_4Sn_4$ at 20 K (χ^2 is a fit quality factor).

Component number	$\lvert\Delta E_Q^{eff}\rvert$ [mm/s]	δ_{IS} [mm/s]	Γ [mm/s]	χ^2
1 (4*e* site)	|2.301(1)|	0.55(2)	0.25*	
2 (2*d* site)	|3.584(1)|	0.53(1)	0.25*	1.298

*Parameter kept constant during the fit.

of the gadolinium sites and the hyperfine parameters. Even for collinear magnetic structures these spectra can be composed of more than one magnetic component. For $Gd_3Cu_4Sn_4$ the magnetic structure as well as the mutual orientations of the principal axes of the EFG tensor at the Gd sites and the magnetic hyperfine field vectors $\boldsymbol{H}_{hf}$ in the crystallographic axes frame are not known, therefore reliable fits of magnetically split spectra are not possible. However, one can get physically reasonable fits under several drastic simplifications.

The fit shown in Fig. 4 at the bottom spectrum, although looks like an ideal one, was obtained under the assumption that the 4.2 K spectrum is composed like that at 20 K of only two magnetic components and with all hyperfine parameters derived from the 20 K spectrum, kept constant. Here, for example, the best fit was obtained with both positive values of the quadrupole interactions constants ΔE_Q while polar angles were kept as $\theta = 90^\circ$ and $\phi = 0^\circ$ for both Gd sites. In turn, similar procedure was used to fit other magnetic spectra, obtained below $T_N = 13$ K where all hyperfine parameters, except that of the magnetic hyperfine field value H_{hf}, were constrained to those obtained for the 4.2 K spectrum. The resulting temperature variation of $H_{hf}(T)$ is displayed in Fig. 5. Although the two last points at 9 and 10 K with a non-zero value of H_{hf} in the lower field $H_{hf}(T)$ dependence can be considered as an artifact of the fitting procedure, however, it cannot be excluded that their non-zero values can be interpreted as a transferred hyperfine field created by magnetic Gd moments located in the magnetic substructure with higher T_N.

It was also shown in other trial fits that the calculated isomer shifts, when treated as free parameters, are always comparable to those obtained above T_N, being not correlated with other parameters. It should be stressed that the derived magnetic hyperfine fields H_{hf}, that can be gained in two component fits, are physically reasonable. The obtained temperature variations of the resulting magnetic hyperfine fields detected below T_N (Fig. 5) point to two magnetic transition temperatures estimated from the Brillouin fits as $T_{N1}^M = 8.4(1)$ K and $T_{N2}^M = 13.5(1)$ K being in accordance with magnetic and heat capacity data. During the Brillouin fit the above-mentioned two last points at the lower curve in Fig. 5 were rejected.

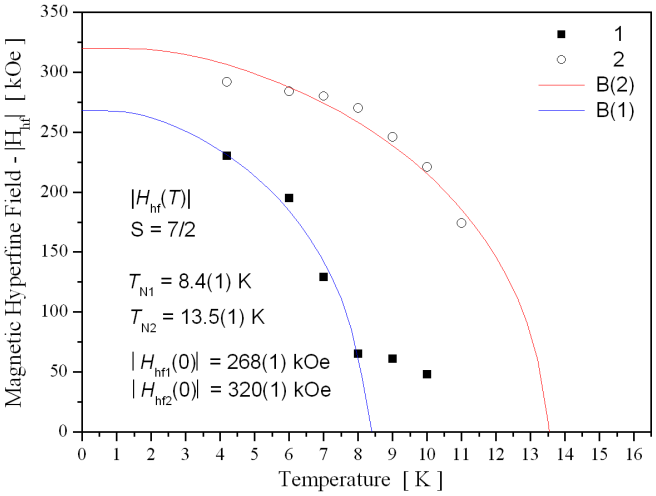

Fig. 5. Temperature evolution of the magnetic hyperfine fields $|H_{\rm hf}|$ at the two gadolinium sites for $Gd_3Cu_4Sn_4$. The continuous lines represent the least-squares fits of the Brillouin function for $S = 7/2$ for both sites. The fits give the estimation for the Néel temperatures $T_{\rm N1}^{\rm M} = 8.4(1)$ and $T_{\rm N2}^{\rm M} = 13.5$ K as well as the absolute values of the saturated magnetic hyperfine fields $|H_{\rm hf1}(0)| = 268(1)$ kOe and $|H_{\rm hf2}(0)| = 320(1)$ kOe, respectively. For explanation see text.

The bigger contribution to the whole spectrum recorded, for example at 4.2 K, has the subspectrum with the lower magnetic hyperfine field (see Fig. 4, bottom spectrum) that can be associated with the 4*e* site having the bigger population of Gd atoms. Hence, the observed magnetic transition around 8.6 K can be interpreted as a transition where the antiferromagnetically coupled 4*e* substructure disorders and consequently close to 13 K an antiferromagnetic to paramagnetic transition takes place owing to the 2*d* substructure disordering. In this context, it is worthy noticing that a smaller number of magnetic moments at the 2*d* position causes smaller magnetic response and this can explain only a small change of the magnetic susceptibility observed around 13 K. These findings confirm that indeed both magnetic Gd substructures order independently, which is in contradiction with the expressed suggestion [3] that the transition at the 8 K event is most likely a spin reorientation.

Acknowledgments

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