Magnetic properties and hyperfine interactions in $EuCu_2Ge_2$ single crystals

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ARTICLE INFO

ABSTRACT

The results of X-ray diffraction, magnetic susceptibility, and ^{151}Eu Mössbauer spectroscopy studies of single crystals of $EuCu_2Ge_2$ grown by a flux method are reported. The magnetic susceptibility and Mössbauer data clearly demonstrate the divalent state of Eu in the temperature range 2–300 K. These data also show that $EuCu_2Ge_2$ is an antiferromagnet with two antiferromagnetic transitions at 5.3(1) and 8.2(1) K in contrast to one antiferromagnetic transition at 13–14 K observed for polycrystalline samples. The direction of the Eu magnetic moment at 2.0 K is 49(2)° away from the c-axis. The Debye temperature of $EuCu_2Ge_2$ determined from the Mössbauer data is 226(2) K. The origin of the differences in magnetic properties of single-crystal and polycrystalline samples of $EuCu_2Ge_2$ is discussed in terms of chemical pressure.

1. Introduction

The intermetallic compounds EuT_2X_2 (T = transition metal, X = Si, Ge) crystallizing in the $ThCr_2Si_2$-type crystal structure [1] (space group $I4/mmm$) exhibit a wealth of interesting magnetic and electronic transport properties [2,3]. Until recently, all these compounds were synthesized in a polycrystalline form. Recently, single crystals of some of these compounds were grown with a flux method [4–9]. Studies of some of these single-crystal compounds revealed that their physical properties are fundamentally different from the properties of their polycrystalline counterparts. For example, polycrystalline $EuCu_2Si_2$ samples show no evidence of magnetic order down to 0.4 K (Refs. [3,10]) and the effective valence of Eu changes from $\sim$2.9 at 4.2 K, to $\sim$2.6 at 300 K, and to $\sim$2.3 at 500 K [10–17]. In contrast, for single-crystal $EuCu_2Si_2$ samples an antiferromagnetic order below $\sim$10 K and a stable divalent configuration of Eu are observed [4,5,18]. For another compound $EuCu_2Ge_2$, one antiferromagnetic transition at $T_N = $ 13–14 K was found for polycrystalline specimens [19,20], whereas for single-crystal samples two antiferromagnetic transitions at $T_{N_1} = 4.0$ K and $T_{N_2} = 8.5$ K (Ref. [5]) and $T_{N_1} = 5.0$ K and $T_{N_2} = 9.0$ K (Ref. [6]) were observed.

The motivation for the present work was to verify the presence of antiferromagnetic ordering and the divalent state of Eu in single-crystal specimens of $EuCu_2Ge_2$ [5,6]. To this end, detailed ^{151}Eu Mössbauer spectroscopy, in addition to magnetic and structural, investigations of single crystals of $EuCu_2Ge_2$ were carried out. We confirm that this compound is an antiferromagnet with two transitions and determine the orientation of the Eu magnetic moment at 2.0 K. We show that Eu atoms are in a stable divalent configuration in the temperature range 2–299 K. In addition, we determine the Debye temperature of this compound.

2. Experimental methods

Single crystals of $EuCu_2Ge_2$ were grown using an In flux method [4–6,21]. High-purity elements of Eu, Cu, and Ge in the stoichiometric ratio were arc melted, placed in an alumina crucible in a 1:15 ratio with In flux, and sealed into an evacuated quartz tube. The crystals were synthesized by heating to 1150 °C at a rate of 300 °C/h, slow cooling down to 650 °C at a rate of 10 °C/h, and decanting off the In flux by means of a high-speed centrifuge.

X-ray diffraction measurements on ground single crystals were performed at 298 K in Bragg–Brentano geometry on the PANalytical X'Pert scanning diffractometer using Cu Kα radiation in the 2θ range 10°–130° in steps of 0.02°. The Kβ line was eliminated by using a Kevex PSi2 Peltier-cooled solid-state Si detector.

The magnetic susceptibility was measured with a Quantum Design magnetic property measurement system in the temperature range 2–300 K.

The ^{151}Eu Mössbauer measurements were conducted using a standard, constant acceleration Mössbauer spectrometer operating in sine mode and a ^{151}Sm (SmF_3) source at room temperature. The 21.5 keV γ-rays were detected with a proportional counter.
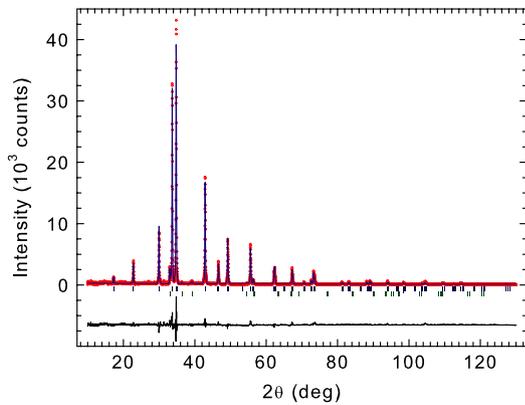

Fig. 1. (Color online) The X-ray diffraction spectrum of the compound $EuCu_2Ge_2$ at 298 K. The experimental data are denoted by open circles, while the line through the circles represents the results of the Rietveld refinement. The upper set of vertical bars represents the Bragg peak positions corresponding to the $EuCu_2Ge_2$ phase, while the lower set refers to the positions of the impurity phase of In (space group $I4/mmm$). The lower solid line represents the difference curve between experimental and calculated spectra.

The spectrometer was calibrated with a Michelson interferometer [22], and the spectra were folded. The Mössbauer absorber consists of a mixture of ground single crystals and boron nitride, which was pressed into a pellet that was put into an Al disk container of thickness 0.008 mm to ensure a uniform temperature over the whole sample. The surface density of the Mössbauer absorber was 27.0 mg/cm^2.

The Mössbauer source ^{151}Sm (SmF$_3$) used is not a monochromatic source as ^{151}Sm nuclei are located in the SmF$_3$ matrix at a site of noncubic symmetry. By measuring the ^{151}Eu Mössbauer spectra of a cubic EuSe compound we determined [23] that the electric quadrupole coupling constant eQ_gV_{zz} (Ref. [24]) in our source is $-3.69(13)$ mm/s [$Q_g = 0.903$ b (Ref. [25])], which is close to the value found in Ref. [26]. The precise shape of the source emission line was taken into account in the fits of the ^{151}Eu Mössbauer spectra. The isomer shift δ of the ^{151}Eu Mössbauer spectra is given here relative to the ^{151}Sm (SmF$_3$) source at room temperature.

3. Experimental results and discussion

3.1. Structural characterization

The ternary compound $EuCu_2Ge_2$ crystallizes in the ThCr$_2$Si$_2$-type crystal structure [1] with the tetragonal space group $I4/mmm$ (No. 139). There are 2 formula units of $EuCu_2Ge_2$ per unit cell. The room-temperature X-ray powder diffraction pattern of $EuCu_2Ge_2$ is shown in Fig. 1. Table 1 lists the structural parameters of $EuCu_2Ge_2$ obtained from the Rietveld refinement [27] of the spectrum in Fig. 1.

The $EuCu_2Ge_2$ specimen contains a small amount of the In flux (space group $I4/mmm$) in the amount of 1.2(3) wt%, as determined from the Rietveld refinement (Fig. 1). The resulting fit of the spectrum in Fig. 1 is reasonably good as judged by the values of χ^2 and the R factors (Table 1). The lattice constants obtained from the Rietveld refinement are $a = 4.2184(4)$ Å and $c = 10.2987(5)$ Å. They should be compared with the lattice constants $a = 4.215$ Å and $c = 10.18$ Å of polycrystalline $EuCu_2Ge_2$ [19]. Clearly, the unit cell volume $V = a^2c$ of a single-crystal specimen (183.3 Å^3) is larger than that of a polycrystalline one [180.9 Å^3 (Ref. [19]) or 179.5 Å^3 (Ref. [20])].

3.2. Magnetic susceptibility

Fig. 2(a) shows the temperature dependence of the magnetic susceptibility χ of $EuCu_2Ge_2$ measured in an applied magnetic field
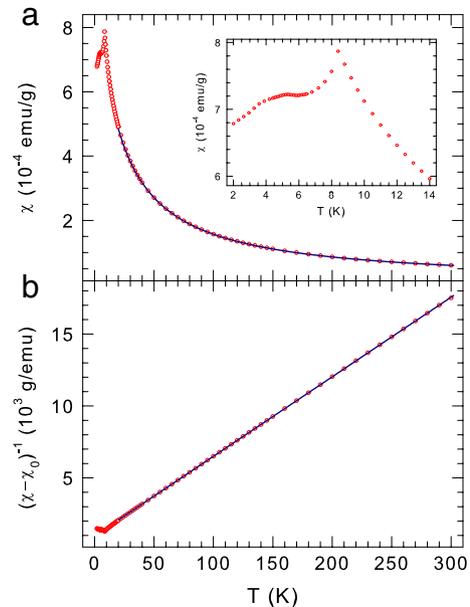

Fig. 2. (Color online) (a) The temperature dependence of the magnetic susceptibility of $EuCu_2Ge_2$, measured in an external magnetic field of 1000 Oe. The solid line is the fit to Eq. (1) in the temperature range 50–300 K, as explained in the text. The inset shows the magnetic susceptibility data in the low-temperature range. (b) The inverse magnetic susceptibility corrected for the contribution χ_0, $(\chi - \chi_0)^{-1}$ versus temperature T. The solid line is the fit to Eq. (1)..

of 1000 Oe. The sample was zero-field cooled to 2.0 K, and the measurements were performed while warming the sample up to 300 K. The $\chi(T)$ curve exhibits a broad peak at 5.3(1) K and a sharp peak at 8.4 K, indicating magnetic ordering of Eu magnetic moments. There are thus two antiferromagnetic transitions at $T_{N_1} = 5.3(1)$ K and $T_{N_2} = 8.4(2)$ K in the single-crystal compound $EuCu_2Ge_2$.

The $\chi(T)$ data above 50 K [Fig. 2(a)] could be fitted to a modified Curie–Weiss law

$$\chi = \chi_0 + \frac{C}{T - \Theta_p}, \tag{1}$$

where χ_0 is the temperature-independent magnetic susceptibility, C is the Curie constant, and Θ_p is the paramagnetic Curie temperature. The Curie constant can be expressed as $C = \frac{N\mu_{eff}^2}{3k_B}$, where N is the number of Eu ions per formula unit, μ_{eff} is the effective magnetic moment, and k_B is the Boltzmann constant. Fig. 2(b) shows the inverse magnetic susceptibility corrected for the contribution χ_0 as $(\chi - \chi_0)^{-1}$ versus temperature; the validity of the modified Curie–Weiss law is evident. The values of χ_0, C, and Θ_p obtained from the fit are, respectively, $3.08(6) \times 10^{-6}$ emu/g, $18.08(2) \times 10^{-3}$ emu K/g, and $-17.6(1)$ K. The value of C corresponds to $\mu_{eff} = 7.83(1)$ μ_B per Eu atom.

For a free Eu^{2+} ion (electronic configuration $^8S_{7/2}$), the theoretical value of $\mu_{eff}^{th} = g\mu_B\sqrt{J(J+1)}$ is 7.94 μ_B [28]. The fact that the experimental value $\mu_{eff} = 7.83(1)$ μ_B is close to the theoretical value of 7.94 μ_B confirms that the magnetic moment is localized on the divalent Eu ions. The negative value of Θ_p indicates the predominantly antiferromagnetic interaction between the Eu^{2+} magnetic moments.

For polycrystalline specimens of $EuCu_2Ge_2$, the peak in the $\chi(T)$ data was observed at 13 K (Ref. [19]) and 14 K [20]. Thus, one antiferromagnetic transition at $T_N = 13$–14 K was found for polycrystalline $EuCu_2Ge_2$ as opposed to two antiferromagnetic transitions at $T_{N_1} = 5.3(1)$ K and $T_{N_2} = 8.4(1)$ K found here. In addition, the value of $\Theta_p = -17.6(1)$ K for single-crystal $EuCu_2Ge_2$

Table 1
Refined structural parameters of $EuCu_2Ge_2$ at 298 K. Space group $I4/mmm$ (No. 139), lattice constants $a = 4.2184(4)$ Å, $c = 10.2987(5)$ Å.

Atom	Site	Point symmetry	Occupancy	x	y	z	B_{iso} (Å^2)
Eu	2a	4/mmm	1.0	0	0	0	0.6(1)
Cu	4d	$\bar{4}$m2	1.0	0	$\frac{1}{2}$	$\frac{1}{4}$	0.3(1)
Ge	4e	4mm	1.0	0	0	0.379(3)	1.2(2)

$R_p = 13.7\%$, $R_{wp} = 11.4\%$, $\chi^2 = 3.2$
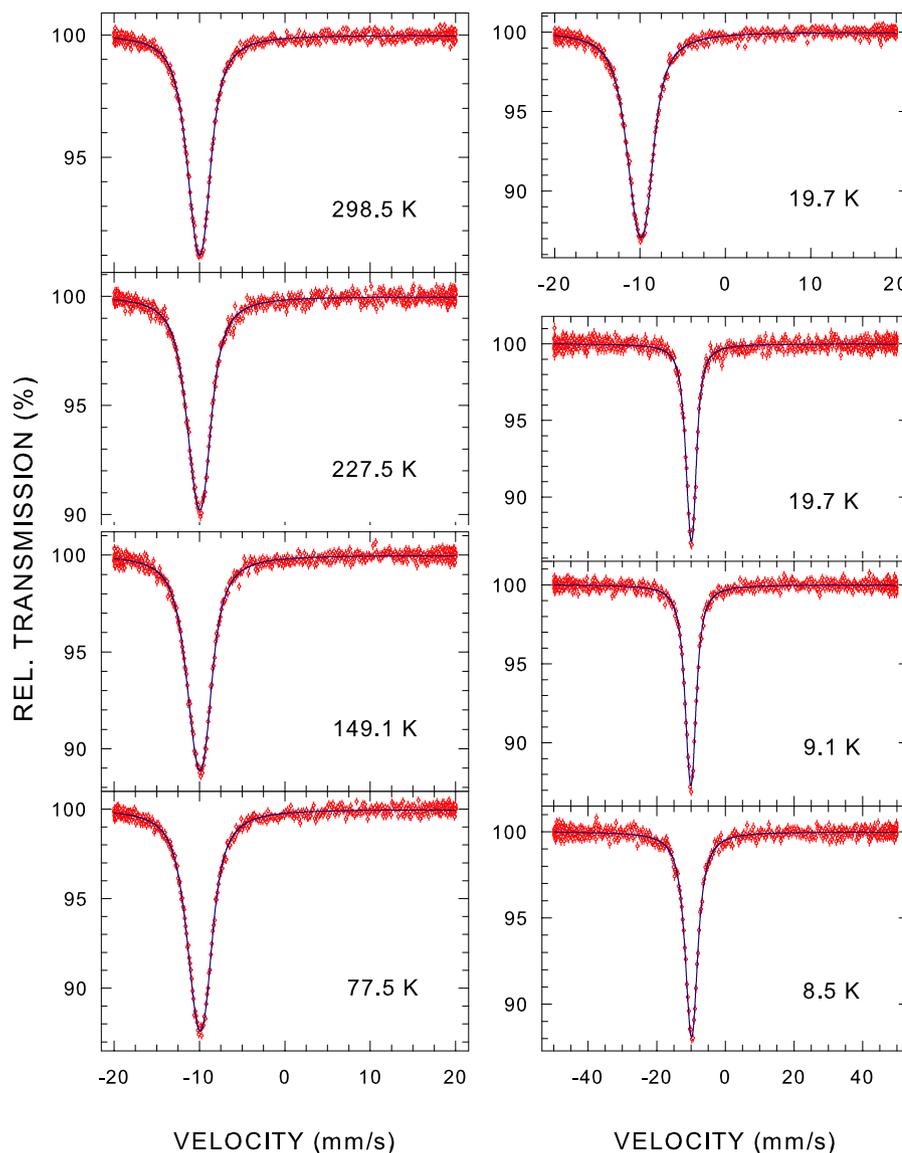
Fig. 3. (Color online) The ^{151}Eu Mössbauer spectra of $EuCu_2Ge_2$ obtained at the indicated temperatures, fitted (solid lines) with an electric quadrupole interaction. The zero-velocity origin is relative to the source.

is higher than the corresponding value for polycrystalline $EuCu_2Ge_2$ [−20 K (Ref. [19]) and −30 K (Ref. [20])]. The value of $\mu_{eff} = 7.83(1)\,\mu_B$ found here is similar to the corresponding value found for polycrystalline $EuCu_2Ge_2$ [8.0 μ_B (Ref. [19]) and 7.8 μ_B (Ref. [20])].

3.3. Mössbauer spectroscopy

The ^{151}Eu Mössbauer spectra of $EuCu_2Ge_2$ recorded at temperatures at which no magnetic dipole hyperfine interaction [24] is present are shown in Fig. 3. These spectra consist of one broad line located at $\delta \approx -10.1$ mm/s. This proves that Eu is divalent [29] in the studied compound.

The Eu atoms are located at the 2a site with point symmetry 4/mmm (Table 1), which ensures a non-zero, axially symmetric (the asymmetry parameter $\eta = 0$) electric field gradient (EFG) tensor at this site, and hence a non-zero electric quadrupole hyperfine interaction. The spectra in Fig. 3 result from a pure electric quadrupole interaction [29]. They were analyzed by means of a least-squares fitting procedure which entailed calculations of the positions and relative intensities of the absorption lines
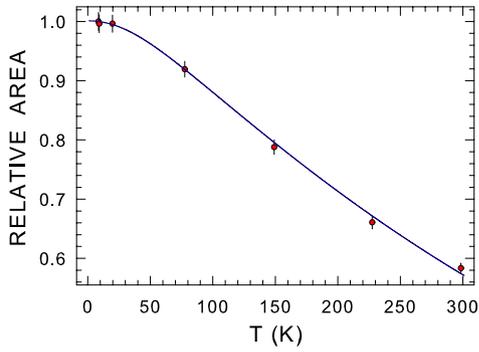
Fig. 4. (Color online) The temperature dependence of the normalized absorption area of the ^{151}Eu Mössbauer spectra in Fig. 4. The solid line is the fit to Eq. (2), as explained in the text.

by numerical diagonalization of the full hyperfine interaction Hamiltonian [24] and the resonance line shape of the spectra was described using a transmission integral formula [30].

The electric quadrupole coupling constant eQ_gV_{zz} derived from the fit of the 298.5 K spectrum (Fig. 3) is 4.77(25) mm/s.

As determined from the fit of other spectra in Fig. 3, it increases approximately linearly with decreasing temperature at the rate of $3.17(20) \times 10^{-3}$ mm/s/K. Such an increase of V_{zz} with decreasing temperature has been observed in various metallic compounds [31]. The value of V_{zz} at the Gd site at 1.4 K in the iso-structural compound GdCu$_2$Si$_2$ is $2.89(5) \times 10^{21}$ V/m^2 (Ref. [32]) and it is reasonably close to the value of $V_{zz} = 4.54(53) \times 10^{21}$ V/m^2 at the Eu site at 1.4 K in EuCu$_2$Ge$_2$ found here.

The absorption area $A(T)$ of a Mössbauer spectrum is proportional to the absorber Debye–Waller factor f_a given [24] by

$$f_a(T) = \exp\left\{ -\frac{3}{4}\frac{E_\gamma^2}{Mc^2k_B\Theta_D}\left[1 + 4\left(\frac{T}{\Theta_D}\right)^2\int_0^{\Theta_D/T}\frac{x\mathrm{d}x}{\mathrm{e}^x - 1}\right]\right\},$$

(2)

where M is the mass of the Mössbauer nucleus, c is the speed of light, E_γ is the energy of the Mössbauer transition, and Θ_D is the Debye temperature. Fig. 4 shows the temperature dependence of the relative area $A(T)/A(T_0)$ ($T_0 = 8.5$ K) derived from the fits of the Mössbauer spectra in Fig. 3. The fit of the relative area (Fig. 4) to Eq. (2) gives $\Theta_D = 226(2)$ K. This value of Θ_D is close to the
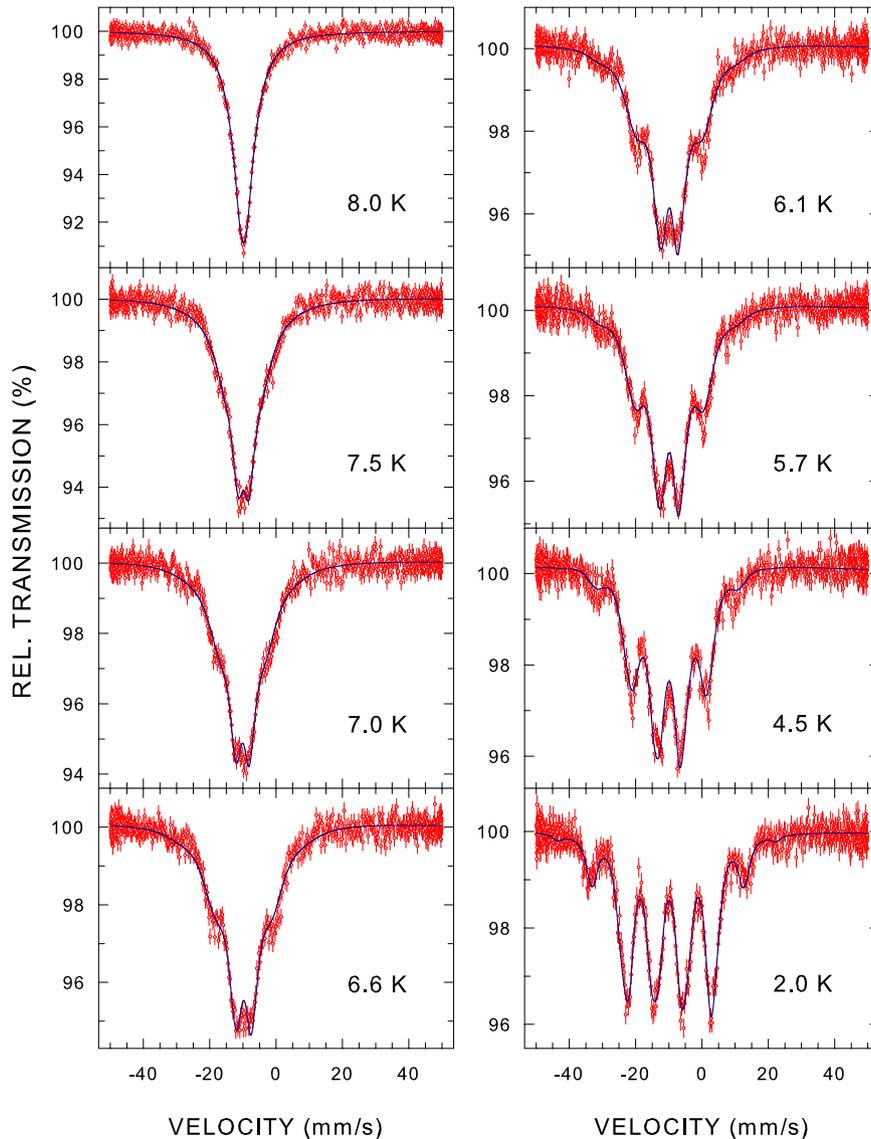

Fig. 5. (Color online) The ^{151}Eu Mössbauer spectra of EuCu$_2$Ge$_2$ obtained at the indicated temperatures, fitted (solid lines) with combined magnetic dipole and electric quadrupole hyperfine interactions, as described in the text. The zero-velocity origin is relative to the source.
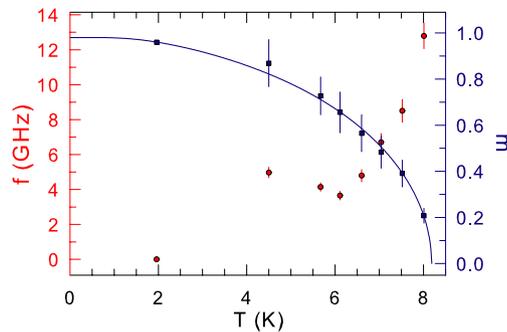
Fig. 6. (Color online) The temperature dependence of the mean jump frequency f and the local order parameter m obtained from the fits of the spectra in Fig. 5 to the uniaxial relaxation model, as described in the text. The solid line is the fit of the $m(T)$ data to a $J = 7/2$ Brillouin function.

value of 210 K found from the specific heat data for polycrystalline $EuCu_2Si_2$ [10].

Fig. 5 shows the ^{151}Eu Mössbauer spectra of $EuCu_2Ge_2$ measured at temperatures at which both magnetic dipole and electric quadrupole hyperfine interactions are present. Similarly to the spectra in Fig. 3, the isomer shift of the spectra in Fig. 5 is $\delta \approx -10.0$ mm/s. This proves that Eu is in a divalent state in the $EuCu_2Ge_2$ compound.

The Mössbauer spectrum at 2.0 K (Fig. 5) results from a static magnetic dipole interaction and an electric quadrupole interaction. It was analyzed in the same way as the spectra in Fig. 3. The following values of the hyperfine parameters were inferred from the fit of this spectrum: $\delta = -9.96(3)$ mm/s, the hyperfine magnetic field $H_{hf} = 318.1(8)$ kOe, $eQ_gV_{zz} = 5.88(93)$ mm/s, and the angle between the direction of H_{hf} and the V_{zz}-axis $\theta = 49(2)°$. As the principal axis of the EFG tensor (V_{zz}-axis) is along the tetragonal c-axis, we conclude that the Eu magnetic moment in $EuCu_2Ge_2$ is aligned $49(2)°$ away from the c-axis. This is consistent with a small anisotropy in the $\chi(T)$ data [5,6].

The Mössbauer spectra at temperatures higher than 2.0 K (Fig. 5) could not be fitted with a simple static Zeeman pattern. A significant enhancement of the inner lines of these spectra clearly indicates that they are spin relaxation spectra resulting from the fluctuations of H_{hf} [33]. These spectra were fitted using the line shape function of the uniaxial relaxation model given by Blume and Tjon [34]. In this model, H_{hf} jumps stochastically between the two directions parallel to the EFG principal axis with frequencies f_+ and f_- [35]. When the magnitude of H_{hf} is constant, one can define a mean jump frequency as $f = (f_+ + f_-)/2$ and a local order parameter as $m = (f_+ - f_-)/2f$. The local order parameter can be regarded as the thermal average of the local magnetic moment $m(T) = \mu(T)/\mu(0)$. In fitting the spectra at temperatures larger than 2.0 K (Fig. 5) to this uniaxial relaxation model, the value of H_{hf} was set at 318.1 kOe obtained from the fit of the 2.0 K spectrum and the fitting parameters were f and m (or equivalently f_+ and f_-), eQ_gV_{zz}, δ, and total absorption (the linewidth was fixed to the value obtained from the fit of the 2.0 K spectrum). As can be seen in Fig. 5, the uniaxial relaxation model reproduces the experimental relaxation spectra of $EuCu_2Ge_2$ satisfactorily.

The temperature dependence of f and m, determined from the fits to the relaxation Mössbauer spectra in Fig. 5, is shown in Fig. 6. One can notice that f increases as temperature approaches T_{N_1} and then again increases dramatically with temperature approaching T_{N_2}. The Néel temperature of the second antiferromagnetic transition is the temperature at which m vanishes. Its value of 8.18(2) K, that was determined from the fit of the $m(T)$ data in Fig. 6 to a $J = 7/2$ Brillouin function, [28] is close to the value of 8.4(2) K determined from the $\chi(T)$ data (Fig. 2). The small changes of f and m around T_{N_1} are suggestive that T_{N_1} is not a real transition but rather a continuous crossover.

Given the striking differences in the physical properties of apparently single-phase single-crystal and polycrystalline specimens of $EuCu_2Ge_2$ and $EuCu_2Si_2$ [4,5,10–14,16,17], a natural question arises as to the source of these differences. One conspicuous difference between the polycrystalline and single-crystal specimens is the unit cell volume V. For the $EuCu_2Si_2$ compound, the values of V for polycrystalline samples are in the range 161.6–165.1 $Å^3$ (Refs. [4,36–38]), whereas for single-crystal specimens they are in the range 166.9–168.5 $Å^3$ [4,5]. For the $EuCu_2Ge_2$ compound, the value of $V = 183.3 Å^3$ for a single-crystal specimen is larger than that for polycrystalline specimens [180.9 $Å^3$ (Ref. [19]) or 179.5 $Å^3$ (Ref. [20])]. It is perhaps this significant difference in V that is one of the sources for the different physical properties of polycrystalline and single-crystal samples of the $EuCu_2Si_2$ and $EuCu_2Ge_2$ compounds. For the $EuCu_2Ge_2$ compound, the lower values of T_N for a single-crystal sample than for a polycrystalline one can be argued to result from a negative chemical pressure [6,39]. As reported by Dionicio, [39] for single-crystal $EuCu_2Ge_2$ samples the value of T_N increases continuously upon applying pressure up to 7.1 GPa. One would thus expect a lower T_N for a large-volume single-crystal specimen than for a small-volume polycrystalline one. Also, the magnetic properties of the EuT_2X_2 compounds are determined by the indirect RKKY exchange interactions between the magnetic Eu ions through conduction electrons. Clearly, these interactions depend on the distance between the Eu ions. Larger values of V for single-crystal samples than for polycrystalline ones mean larger separations between Eu ions in the former, and thus different magnetic behavior.

4. Conclusions

We have reported the results of X-ray diffraction, magnetic susceptibility, and ^{151}Eu Mössbauer spectroscopy measurements of $EuCu_2Ge_2$ single crystals grown from an In flux. We find that Eu atoms are in a stable divalent state in the temperature range 2–300 K. The studied compound is confirmed to be an antiferromagnet with two antiferromagnetic transitions at 5.3(1) and 8.2(1) K, in contrast to one antiferromagnetic transition at 13–14 K found for polycrystalline specimens. The Eu magnetic moments at 2.0 K are directed $49(2)°$ away from the c-axis. The source of the differences in magnetic properties of single-crystal and polycrystalline samples of $EuCu_2Ge_2$ is discussed in terms of chemical pressure. The Debye temperature of $EuCu_2Ge_2$ is found to be 226(2) K.

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