PHYSICAL REVIEW B **82**, 134404 (2010)

Spin-glass ordering and absence of valence fluctuations of Eu in $EuCu_2Si_2$ single crystals

P. Wang,[1] Z. M. Stadnik,[1,*] J. Żukrowski,[2] B. K. Cho,[3] and J. Y. Kim[3]
[1]*Department of Physics, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5*
[2]*Solid State Physics Department, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, 30-059 Kraków, Poland*
[3]*Department of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, South Korea*

(Received 6 June 2010; revised manuscript received 5 September 2010; published 5 October 2010)

The results of x-ray diffraction, dc and ac magnetic susceptibilities, and ^{151}Eu Mössbauer spectroscopy studies of single crystals of $EuCu_2Si_2$ grown by a flux method are reported. The magnetic susceptibility and Mössbauer data clearly demonstrate the divalent state of Eu in the temperature range 1.9–298.2 K, in contrast to an intermediate-valence state of Eu observed for polycrystalline samples. These data also show that, contrary to earlier reports, the $EuCu_2Si_2$ compound is a spin glass.

DOI: 10.1103/PhysRevB.82.134404 PACS number(s): 74.70.−b, 76.80.+y

I. INTRODUCTION

The ternary compound $EuCu_2Si_2$ is one of the first Eu-based compounds in which the valence fluctuation phenomenon was observed.[1] It is also one of the most thoroughly studied.[2–17] Previous experimental investigations showed[2,4,6,8–11,17] that the effective valence of Eu in $EuCu_2Si_2$ changes from ~2.9 at 4.2 K, to ~2.6 at 300 K, and to ~2.3 at 500 K. The ternary compound $EuCu_2Si_2$ shows no magnetic ordering down to 0.4 K.[2] All the experimental studies mentioned above were carried out on $EuCu_2Si_2$ in a polycrystalline form.

Recently, single crystals of $EuCu_2Si_2$ were synthesized[18,19] for the first time via an In flux method.[20] Astonishingly, magnetic susceptibility, electron spin resonance, and specific-heat data[18,19] are consistent with Eu being in a stable divalent state in this compound. In addition, the presence of antiferromagnetic ordering below ~10 K in this compound was deduced from the magnetic susceptibility data.[18,19]

In this paper, we report on the results of magnetic and ^{151}Eu Mössbauer spectroscopy (MS) investigations of single crystals of $EuCu_2Si_2$. We show unambiguously that this compound is a spin glass and that there are no charge fluctuations of Eu, i.e., that Eu atoms are in a stable divalent state in the temperature range 1.9–298 K. A possible reason is suggested for the diametrically different physical properties of apparently single-phase polycrystalline and single-crystal $EuCu_2Si_2$ compounds.

II. EXPERIMENTAL METHODS

Single crystals of $EuCu_2Si_2$ were grown using an In flux method.[20] High-purity elements of Eu, Cu, and Si 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 PANanalytical X'Pert scanning diffractometer using Cu $K\alpha$ radiation in the 2θ range $10°-130°$ in steps of 0.02°. The $K\beta$ line was eliminated by using a Kevex PSi2 Peltier-cooled solid-state Si detector.

The dc and ac magnetic susceptibilities were measured on ground single crystals using a Quantum Design magnetic property measurement system (MPMS-XL7). The ac magnetic susceptibility data were collected in a 1 Oe ac magnetic field and zero external magnetic field for frequencies varying from 3 to 1000 Hz.

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. The spectrometer was calibrated with a 6.35-μm-thick α-Fe foil[21] and the spectra were folded. The Mössbauer absorber consisted 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 of 0.008 mm to ensure a uniform temperature over the whole sample. The surface density of the Mössbauer absorber was 34.1 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[22] that the electric quadrupole coupling constant eQ_gV_{zz} (Ref. 23) in our source is −3.69(13) mm/s [Q_g =0.903 b (Ref. 24)], which is close to the value found in Ref. 25. 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.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Structural characterization

The ternary compound $EuCu_2Si_2$ crystallizes in the $ThCr_2Si_2$-type crystal structure[26] with the tetragonal space group *I*4/*mmm* (No. 139). There are 2 formula units of

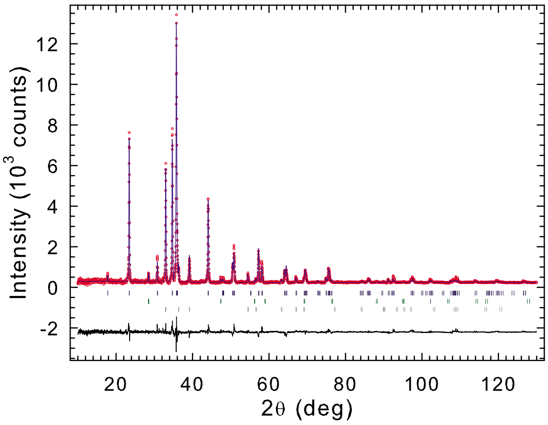

FIG. 1. (Color online) The x-ray diffraction spectrum of the compound $EuCu_2Si_2$ at 298 K. The experimental data are denoted by open circles, while the line through the circles represents the results of the Rietveld refinement. The upper set of vertical bars represents the Bragg peak positions corresponding to the $EuCu_2Si_2$ phase while the lower two sets refer to the positions of the impurity phases of Si (space group $Fd\bar{3}m$) and In (space group $I4/mmm$). The lower solid line represents the difference curve between experimental and calculated spectra.

$EuCu_2Si_2$ per unit cell. The room-temperature x-ray powder-diffraction pattern of $EuCu_2Si_2$ is shown in Fig. 1. Table I lists the structural parameters of $EuCu_2Si_2$ obtained from the Rietveld refinement[27] of the spectrum in Fig. 1.

The $EuCu_2Si_2$ specimen contains a small amount of a second phase of unreacted Si and of the In flux (Fig. 1). The presence of a minor amount of the second phase of Si suggests that a small deviation from the ideal composition $EuCu_2Si_2$ might occur. Attempts at refining the occupancies of Eu, Cu, and Si did not result in values different from 1.0 (Table I). The resulting fit of the spectrum in Fig. 1 is reasonably good as judged by the values of χ^2 and R factors (Table I). The lattice constants obtained from the Rietveld refinement, $a=4.1106(3)$ Å and $c=9.9853(4)$ Å, compare well with the values reported earlier.[18,19]

B. Magnetic susceptibility

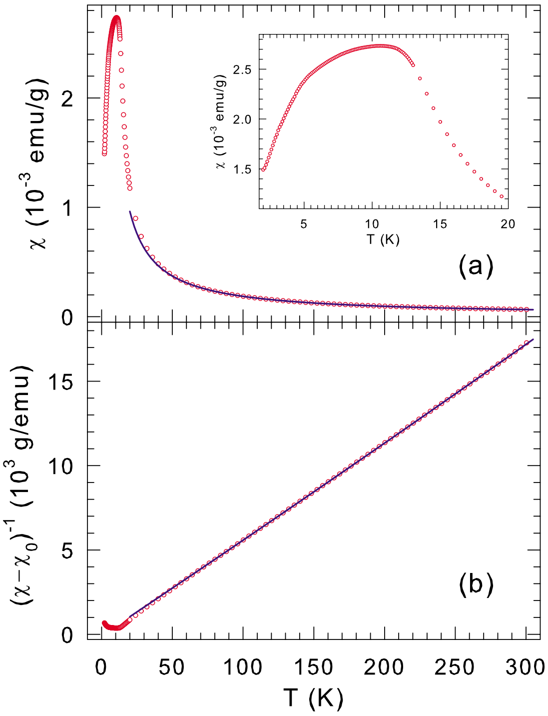

FIG. 2. (Color online) (a) The temperature dependence of the ZFC magnetic susceptibility of $EuCu_2Si_2$, measured in an external magnetic field of 1000 Oe. The solid line is the fit to Eq. (1) in the temperature range 80–300K, as explained in the text. The inset shows the magnetic susceptibility data 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).

The temperature dependence of the magnetic susceptibility χ of $EuCu_2Si_2$ measured in an applied magnetic field of 1000 Oe is shown in Fig. 2(a). The sample was zero-field cooled (ZFC) 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 10.6(1) K, indicating magnetic ordering of Eu magnetic moments. The $\chi(T)$ data, corrected for the diamagnetic contribution from the In and Si impurities, could be fitted above 80 K to a modified Curie-Weiss law

$$\chi=\chi_0+\frac{C}{T-\Theta_p}, \qquad (1)$$

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 Boltz-

TABLE I. Refined structural parameters of $EuCu_2Si_2$ at 298 K. Space group $I4/mmm$ (No. 139), lattice constants $a=4.1106(3)$ Å and $c=9.9853(4)$ Å.

Atom	Site	Point symmetry	Occupancy	x	y	z	B_{iso} (Å^2)
Eu	$2a$	$4/mmm$	1.0(1)	0	0	0	0.3(1)
Cu	$4d$	$\bar{4}m2$	1.0(1)	0	$\frac{1}{2}$	$\frac{1}{4}$	1.1(2)
Si	$4e$	$4mm$	1.0(1)	0	0	0.373(3)	0.7(1)
$R_p=7.82\%$, $R_{wp}=9.13\%$, $\chi^2=1.75$							

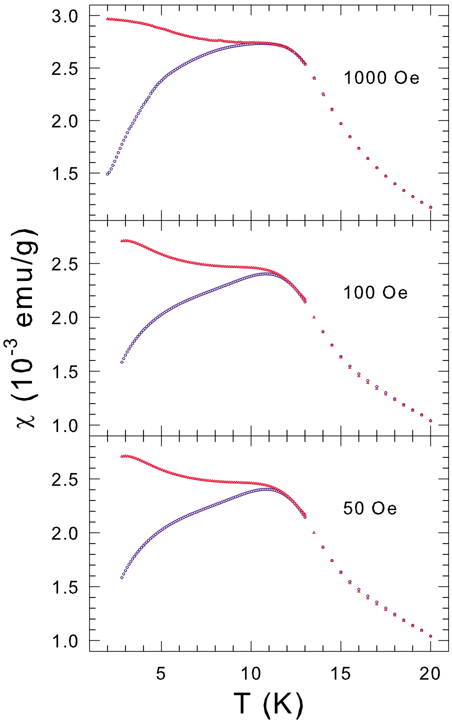

FIG. 3. (Color online) The temperature dependence of the ZFC (○) and FC (△) magnetic susceptibility of $EuCu_2Si_2$ measured in various external magnetic fields.

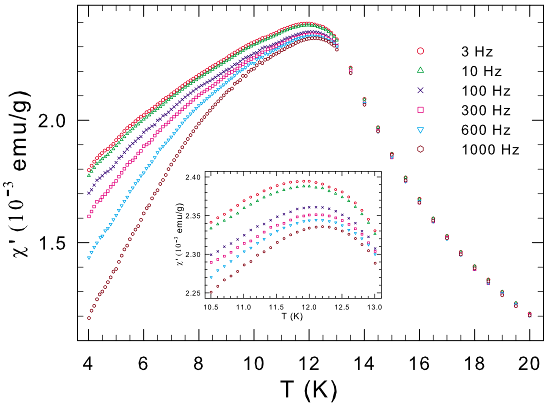

FIG. 4. (Color online) The temperature dependence of the real part of the ac magnetic susceptibility of $EuCu_2Si_2$ measured for different applied frequencies from 3 to 1000 Hz. The inset is a magnification around the maximum χ'.

mann constant. Figure 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, $7.20(8)\times10^{-6}$ emu/g, $22.44(3)\times10^{-3}$ emu K/g, and 1.37(8) K. The value of C corresponds to $\mu_{eff}=7.76(1)$ 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 $\mu_{eff}=7.76(1)$ 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. A small and positive value of Θ_p indicates the predominantly ferromagnetic interaction between the Eu^{2+} magnetic moments. Clearly, one would expect a negative value of Θ_p if the Eu magnetic moments ordered antiferromagnetically below 10.6 K.

Figure 3 shows the temperature dependence of the ZFC and field-cooled (FC) magnetic susceptibility of $EuCu_2Si_2$ measured in applied magnetic fields of 1000, 100, and 50 Oe. The occurrence of a bifurcation between the ZFC and FC data is evident. This proves that the studied compound is a spin glass.[29] In addition, the temperature at which the bifurcation occurs shifts toward lower values with the increase in the applied magnetic field. This behavior is one of the properties of a spin-glass system.[29]

The temperature dependence of the real part χ' of the ac magnetic susceptibility of $EuCu_2Si_2$ for selected frequencies between 3 and 1000 Hz is shown in Fig. 4. The $\chi'(T)$ curves show maxima whose amplitudes and positions depend on the frequency f of the applied ac magnetic field. With increasing frequency, the peak positions are shifted to higher temperatures and the peak intensity of $\chi'(T)$ decreases. These features are typical for canonical spin glasses.[29] The position of the maximum in $\chi'(T)$ can be used to define the freezing temperature T_f. Below the maximum in $\chi'(T)$, the magnitude of χ' is frequency dependent but it becomes independent of frequency at temperature just above T_f. This behavior is qualitatively similar to that of canonical spin glasses.[29]

The temperature (T_f) of the maximum in $\chi'(T)$ (Fig. 4) was determined from a curve fitting procedure. The frequency dependence of T_f is shown in Fig. 5. A quantitative measure of the change in the freezing temperature with frequency in spin glasses is represented by the relative change in T_f per decade change in f defined as[29]

$$K=\frac{\Delta T_f}{T_f\Delta\log f}. \qquad (2)$$

From a linear fit of the data in Fig. 5 and using the average value of $T_f=12.06$ K for the range of frequencies used, one finds that $K=0.0084(6)$. This value is a factor of about two greater than that found for such canonical spin glasses as $Cu_{1-x}Mn_x$ $(K=0.005)$ and $Au_{1-x}Mn_x$ $(K=0.0045)$ but compa-

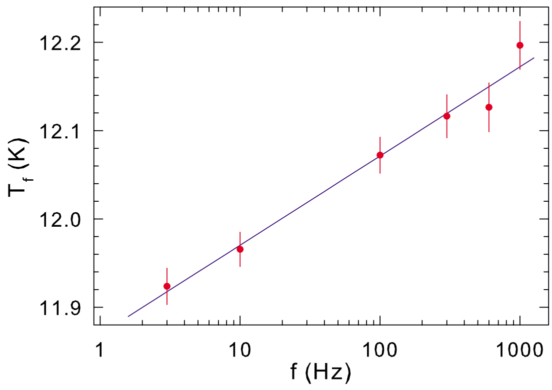

FIG. 5. (Color online) The frequency dependence of the freezing temperature T_f of $EuCu_2Si_2$. The solid line is the best linear fit to the T_f data.

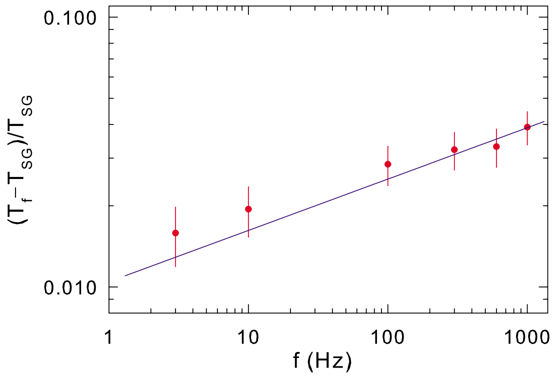

FIG. 6. (Color online) The frequency dependence of the freezing temperature T_f of $EuCu_2Si_2$. The solid line is the best linear fit to Eq. (3).

rable to that of several other canonical spin glasses such as $Ag_{1-x}Mn_x$ ($K=0.006$) and $Au_{1-x}Fe_x$ ($K=0.010$).[29]

The frequency-dependent maximum of $\chi'(T)$ indicates the freezing temperature T_f, where the maximum relaxation time, τ, of the system is equal to the characteristic time $1/f$ set by the frequency of the ac-susceptibility measurement. The relaxation time $\tau=1/f$ of magnetic moments will show a critical slowing down when approaching T_f from above, characterized by a power law $\tau \propto \xi^z$, where ξ is the correlation length and z is the dynamic scaling exponent.[30] The correlation length ξ itself is related to the reduced temperature $t=(T_f-T_{SG})/T_{SG}$ as $\xi \propto t^{-\nu}$, where T_{SG} is the phase-transition temperature and ν is the critical correlation-length exponent.[30] Therefore, the temperature dependence of f obeys the power-law divergence[29,30]

$$f = f_0 \left(\frac{T_f - T_{SG}}{T_{SG}} \right)^{z\nu}, \quad T_f > T_{SG}, \tag{3}$$

where f_0 is the microscopic relaxation time. The best fit of the $T_f(f)$ data to Eq. (3) (Fig. 6) gives $f_0=2.57(29) \times 10^{11}$ Hz, $T_{SG}=11.74(13)$ K, and $z\nu=5.26(86)$. The derived values of f_0 and $z\nu$ are similar to those found for many different spin glasses.[29,31]

C. Mössbauer spectroscopy

The ^{151}Eu Mössbauer spectra of $EuCu_2Si_2$ recorded at temperatures at which no magnetic dipole hyperfine interaction[23] is present are shown in Fig. 7. In contrast to the Mössbauer spectra of polycrystalline $EuCu_2Si_2$ (Refs. 1, 8, and 12), the spectra of the studied single-crystal specimen consist of one line located at $\delta \approx -8.7$ mm/s. This proves that Eu is divalent[32] and that there are no signs of valence fluctuations in the temperature range 14.8–298.2 K.

The spectra in Fig. 7 result from a pure electric quadrupole interaction.[32] They were analyzed by means of a least-squares fitting procedure which entailed calculations of the positions and relative intensities of the absorption lines by numerical diagonalization of the full hyperfine interaction Hamiltonian[23] and the resonance line shape of the spectra was described using a transmission integral formula.[33]

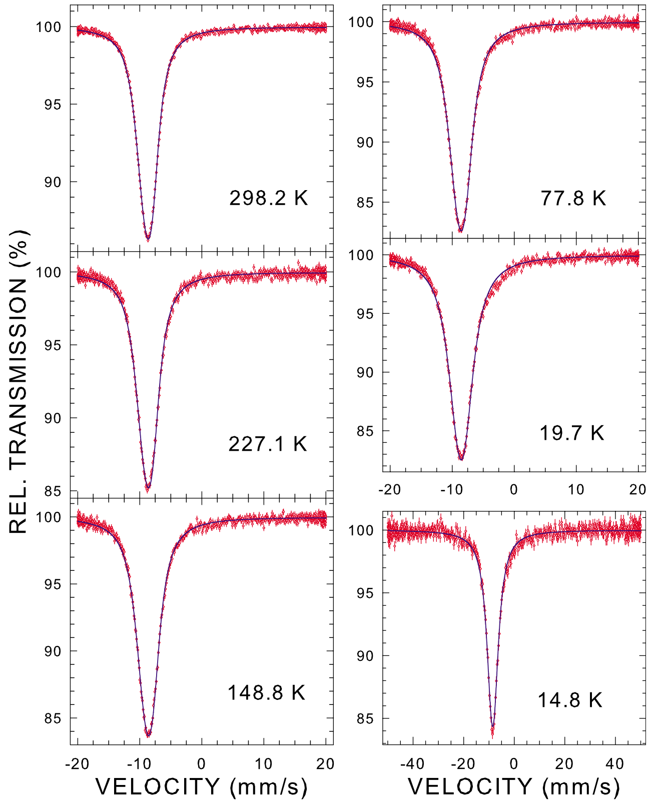

FIG. 7. (Color online) The ^{151}Eu Mössbauer spectra of $EuCu_2Si_2$ obtained at the indicated temperatures, fitted (solid lines) with an electric quadrupole interaction. The zero-velocity origin is relative to the source.

The electric quadrupole coupling constant eQ_gV_{zz} derived from the fit of the 298.2 K spectrum (Fig. 7) is 5.892(140) mm/s. As determined from the fit of other spectra in Fig. 7, it increases linearly with decreasing temperature at the rate of $3.10(15) \times 10^{-3}$ mm/s/K. The absorption area $A(T)$ of a Mössbauer spectrum is proportional to the absorber Debye-Waller factor f_a given[23] by

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

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. Figure 8 shows the temperature dependence of the relative area $A(T)/A(T_0)$ ($T_0 = 14.8$ K) derived from the fits of the Mössbauer spectra in Fig. 7. The fit of the relative area (Fig. 8) to Eq. (4) gives $\Theta_D=233(1)$ K. This value of Θ_D is close to the value of 210 K found from the specific heat data for polycrystalline $EuCu_2Si_2$.[2]

Figure 9 shows the ^{151}Eu Mössbauer spectra of $EuCu_2Si_2$ measured at temperatures at which both magnetic dipole and electric quadrupole hyperfine interactions are present. Similarly to the spectra in Fig. 7, the isomer shift of the spectra in Fig. 9 is $\delta \approx -8.6$ mm/s. This conclusively proves that Eu is

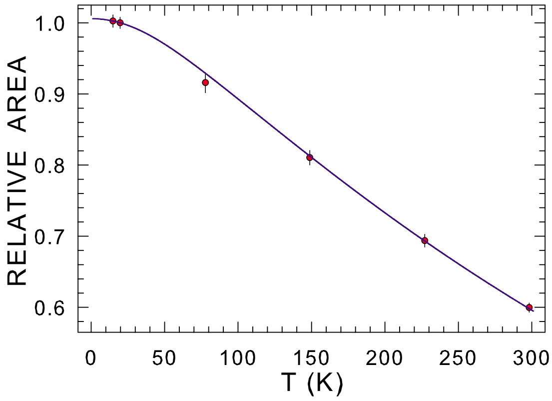

FIG. 8. (Color online) The temperature dependence of the normalized absorption area of the ^{151}Eu Mössbauer spectra in Fig. 4. The solid line is the fit to Eq. (4), as explained in the text.

divalent in the temperature range 1.9–298.2 K, i.e., there are no Eu valence fluctuations in the $EuCu_2Si_2$ compound.

The Mössbauer spectra at 1.9 and 4.4 K (Fig. 9) result from a static magnetic dipole interaction and an electric quadrupole interaction. The values of the hyperfine magnetic field H_{hf} and eQ_gV_{zz} obtained from the fit of these spectra, which involved the numerical diagonalization of the full hyperfine interaction Hamiltonian,[23] are 403.2(1.1) kOe, 6.710(202) mm/s and 386.4(1.2) kOe, 6.822(197) mm/s, respectively.

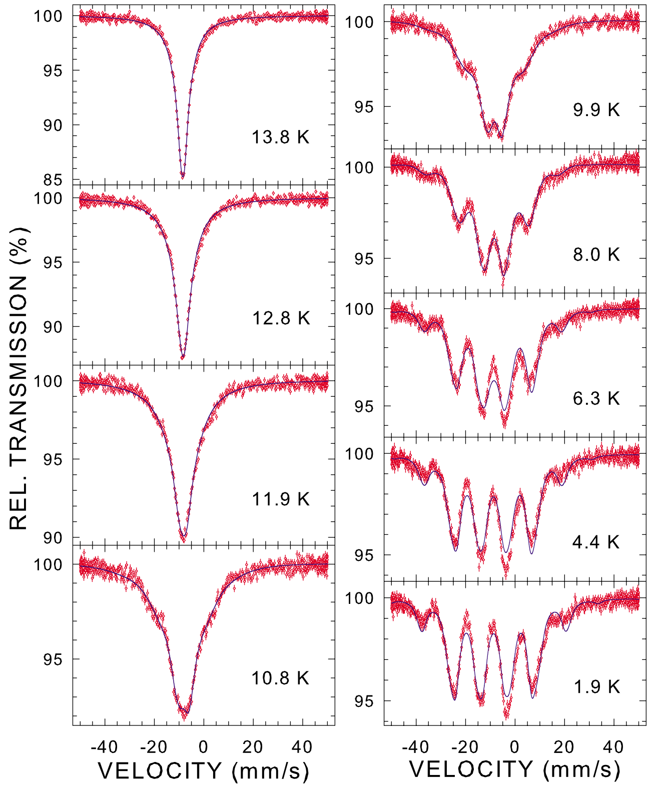

FIG. 9. (Color online) The ^{151}Eu Mössbauer spectra of $EuCu_2Si_2$ obtained at the indicated temperatures, fitted (solid lines) with combined magnetic dipole and electric quadrupole hyperfine interactions, as described in the text. The zero-velocity origin is relative to the source.

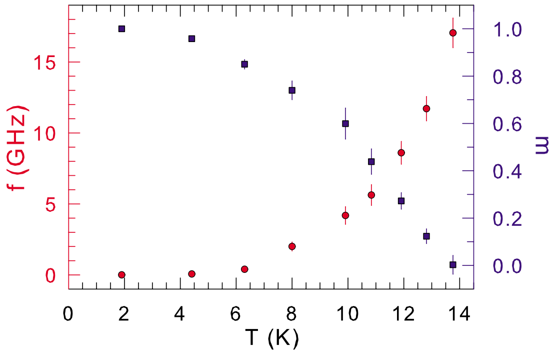

FIG. 10. (Color online) The temperature dependence of the mean jump frequency f and the local order parameter m obtained from the fits of the spectra in Fig. 9 to the uniaxial relaxation model, as described in the text.

The Mössbauer spectra at temperatures higher than 4.4 K (Fig. 9) 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}.[34] These spectra were fitted using the line shape function of the uniaxial relaxation model given by Blume and Tjon.[35] In this model, H_{hf} jumps stochastically between the two directions parallel to the electric field gradient principal axis with frequencies f_+ and f_-.[36] 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 4.4 K (Fig. 9) to this uniaxial relaxation model, the value of H_{hf} was set at 386.4 kOe 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 4.4 K spectrum). As can be seen in Fig. 9, the uniaxial relaxation model reproduces the experimental relaxation spectra of $EuCu_2Si_2$ satisfactorily. The temperature dependence of f and m, determined from the fits to the Mössbauer spectra in Fig. 9, is shown in Fig. 10.

The temperature at which m vanishes, that was estimated from the spline extrapolation of the $m(T)$ data in Fig. 10, is 13.82(15) K. If one defines the freezing temperature of a spin glass determined from MS, T_f^M, as the temperature at which the local order parameter disappears, then $T_f^M = 13.82(15)$ K. Clearly, T_f^M is significantly larger than the freezing temperature $T_{SG}=11.74(13)$ K determined from the ac magnetic susceptibility data. The systematically higher values of T_f^M than T_{SG} have been observed for many other spin-glass systems.[29,37] The inequality $T_f^M > T_{SG}$ results from the time window τ_{exp} of the experimental technique used to determine the freezing temperature. For MS, τ_{exp} is given by the Larmor precession time τ_L ($\tau_L \equiv \omega_L^{-1} = \frac{\hbar I_{ex}}{H_{hf}\mu_{ex}}$, where ω_L is the angular Larmor frequency, and I_{ex} and μ_{ex} are the spin and the magnetic moment of the excited nuclear state, respectively[38]) of the nuclear magnetic moment in the hyperfine magnetic field. In the case studied here, $\tau_L = 7.3 \times 10^{-10}$ s ($f_L = 0.22$ GHz) for $H_{hf} = 386.4$ kOe at 4.4 K. With a wide distribution of the relaxation times τ of fluctuating spin clusters in a spin glass,[29,37,39] those clusters fluctuating with τ larger than τ_{exp} for a given experimental technique will appear frozen and will be discerned at a higher temperature than by an experimental technique characterized by a smaller τ_{exp}. Thus, one expects to observe an increase of T_{SG} with decreasing τ_{exp}, which is indeed universally observed in spin glasses.[29,37]

It is rather intriguing to observe diametrically different physical properties of apparently single-phase polycrystalline[1–17] and single-crystal[18,19] samples of the $EuCu_2Si_2$ compound. One conspicuous difference between the polycrystalline and single-crystal specimens is the unit-cell volume $V=a^2c$. The values of V for polycrystalline samples [163.3 Å^3 (Ref. 12), 163.3 Å^3 (Ref. 14), 164.0 Å^3 (Ref. 15), 165.8 and 163.4 Å^3 (Ref. 18), 165.1 Å^3 (Ref. 40), 161.6 Å^3 (Ref. 41), and 163.1 Å^3 (Ref. 42)] are systematically smaller than those for single-crystal specimens [168.5 Å^3 (Ref. 18), 166.9 Å^3 (Ref. 19), and 168.7 Å^3 (Table I)]. It is perhaps this significant difference in V that is responsible for the different physical properties of polycrystalline and single-crystal samples of the $EuCu_2Si_2$ compound.

IV. CONCLUSIONS

We have reported the results of x-ray diffraction, dc and ac magnetic susceptibilities, and ^{151}Eu Mössbauer spectroscopy measurements of $EuCu_2Si_2$ single crystals grown from an In flux. We find that Eu atoms are in a stable divalent state in the temperature range 1.9–298.2 K. The studied compound is shown to be a spin glass with a freezing temperature of 11.74(13) K. The Debye temperature of $EuCu_2Si_2$ is found to be 233(1) K.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada. The work at GIST was supported by the Korea Science and Engineering Foundation (KOSEF) NCRC grant funded by the MEST (Grant No. R15-2008-006-01002-0).

---

*stadnik@uottawa.ca

[1] E. R. Bauminger, D. Froindlich, I. Nowik, S. Ofer, I. Felner, and I. Mayer, Phys. Rev. Lett. **30**, 1053 (1973).

[2] B. C. Sales and R. Viswanathan, J. Low Temp. Phys. **23**, 449 (1976).

[3] K. H. J. Buschow, M. Campagna, and G. K. Wertheim, Solid State Commun. **24**, 253 (1977).

[4] E. V. Sampathkumaran, L. C. Gupta, and R. Vijayaraghavan, Phys. Rev. Lett. **43**, 1189 (1979).

[5] T. K. Hatwar, R. M. Nayak, B. D. Padalia, M. N. Ghatikar, E. V. Sampathkumaran, L. C. Gupta, and R. Vijayaraghavan, Solid State Commun. **34**, 617 (1980).

[6] S. H. Devare, H. G. Devare, and J. A. Cameron, J. Phys. C **14**, 1491 (1981).

[7] L. C. Gupta, E. V. Sampathkumaran, R. Vijayaraghavan, V. Prabhawalkar, P. D. Prabhawalkar, and B. D. Padalia, Phys. Rev. B **23**, 4283 (1981).

[8] J. Röhler, D. Wohlleben, G. Kaindl, and H. Balster, Phys. Rev. Lett. **49**, 65 (1982).

[9] A. Scherzberg, Ch. Sauer, U. Köbler, W. Zinn, and J. Röhler, Solid State Commun. **49**, 1027 (1984).

[10] E. M. Levin, JETP Lett. **42**, 297 (1985).

[11] G. Neumann, J. Langen, H. Zahel, D. Plümacher, Z. Kletowski, W. Schlabitz, and D. Wohlleben, Z. Phys. B **59**, 133 (1985).

[12] M. M. Abd-Elmeguid, Ch. Sauer, and W. Zinn, J. Phys. C **18**, 345 (1985).

[13] E. Zirngiebl, S. Blumenröder, G. Güntherodt, and E. V. Sampathkumaran, J. Magn. Magn. Mater. **54-57**, 343 (1986).

[14] A. Palenzona, S. Cirafici, and F. Canepa, J. Less Common Met. **119**, 199 (1986).

[15] Y. Takigawa, S. Noguchi, and K. Okuda, J. Magn. Magn. Mater. **76-77**, 345 (1988).

[16] E. M. Levin, B. S. Kuzhel, O. I. Bodak, B. D. Belan, and I. N. Stets, Phys. Status Solidi B **161**, 783 (1990).

[17] P. A. Alekseev, R. V. Chernikov, K. V. Klementiev, V. N. Lazukov, and A. P. Menushenkov, Nucl. Instrum. Methods Phys. Res. A **543**, 202 (2005).

[18] P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, M. F. Hundley, M. S. Sercheli, R. R. Urbano, C. Rettori, Z. Fisk, and S. B. Oseroff, Phys. Rev. B **63**, 092406 (2001).

[19] J. S. Rhyee, B. K. Cho, and H. C. Ri, J. Appl. Phys. **93**, 8346 (2003).

[20] P. C. Canfield and Z. Fisk, Philos. Mag. B **65**, 1117 (1992); P. C. Canfield and I. R. Fisher, J. Cryst. Growth **225**, 155 (2001).

[21] *Certificate of Calibration in Iron Foil Mössbauer Standard*, Natl. Bur. Stand. (U.S.) Circ. No. 1541, edited by J. P. Cali (U.S. GPO, Washington, D.C., 1971).

[22] Z. M. Stadnik and J. Żukrowski (unpublished).

[23] N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy* (Chapman and Hall, London, 1971); P. Gütlich, R. Link, and A. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry* (Springer, Berlin, 1978).

[24] Y. Tanaka, R. M. Steffen, E. B. Shera, W. Reuter, M. V. Hoehn, and J. D. Zumbro, Phys. Rev. C **29**, 1830 (1984).

[25] I. Nowik and I. Felner, Hyperfine Interact. **28**, 959 (1986).

[26] W. Rieger and E. Parthé, Monatsch. Chem. **100**, 444 (1969).

[27] R. A. Young, *The Rietveld Method* (Oxford University Press, Oxford, 1993).

[28] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).

[29] J. A. Mydosh, *Spin Glasses: An Experimental Introduction* (Taylor & Francis, London, 1993).

[30] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[31] J. Souletie and J. L. Tholence, Phys. Rev. B **32**, 516 (1985).

[32] F. Grandjean and G. J. Long, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, edited by G. J. Long and F. Grandjean (Plenum, New York, 1989), Vol. 3, p. 513.

[33] S. Margulies and J. R. Ehrman, Nucl. Instrum. Methods **12**, 131 (1961); G. K. Shenoy, J. M. Friedt, H. Maletta, and S. L. Ruby, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman, C. W. Seidel, and D. K. Dieterly (Plenum, New York, 1974), Vol. 10, p. 277.

[34] F. J. Litterst, J. M. Friedt, J. L. Tholence, and F. Holtzberg, J. Phys. C **15**, 1049 (1982).

[35] M. Blume and J. A. Tjon, Phys. Rev. **165**, 446 (1968).

[36] D. G. Rancourt, in *Mössbauer Spectroscopy Applied to Magnetism and Materials Science*, edited by G. J. Long and F. Grandjean (Plenum, New York, 1996), Vol. 2, p. 105.

[37] A. P. Murani, J. Magn. Magn. Mater. **5**, 95 (1977); **22**, 271 (1981); H. G. Wagner and U. Gonser, *ibid.* **31-34**, 1343 (1983); C. Meyer, F. Hartmann-Boutron, Y. Gros, and I. A. Campbell, *ibid.* **46**, 254 (1985); H. Aruga, T. Tokoro, and A. Ito, J. Phys. Soc. Jpn. **57**, 261 (1988); J. Bogner, M. Reissner, W. Steiner, and S. M. Dubiel, J. Phys.: Condens. Matter **10**, 9849 (1998).

[38] J. G. Stevens, in *CRC Handbook of Spectroscopy*, edited by J. W. Robinson (CRC Press, Boca Raton, 1981), Vol. III, p. 403.

[39] L. Lundgren, P. Svedlindh, and O. Beckman, J. Phys. F **12**, 2663 (1982).

[40] S. Patil, R. Nagarajan, C. Godart, J. P. Kappler, L. C. Gupta, B. D. Padalia, and R. Vijayaraghavan, Phys. Rev. B **47**, 8794 (1993).

[41] I. Mayer, J. Cohen, and I. Felner, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. (Suppl.) **28**, S102 (1972).

[42] W. Schlabitz, J. Baumann, G. Neumann, D. Plümacher, and K. Reggentin, in *Crystalline Electric Field Effects in f-Electron Magnetism*, edited by R. P. Guertin, W. Suski, and Z. Zołnierek (Plenum, New York, 1982), p. 289.