Spin-glass ordering and absence of valence fluctuations of Eu in EuCu₂Si₂ single crystals

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The results of x-ray diffraction, dc and ac magnetic susceptibilities, and ¹⁵¹Eu Mössbauer spectroscopy studies of single crystals of EuCu₂Si₂ 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 EuCu₂Si₂ compound is a spin glass.

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I. INTRODUCTION

The ternary compound EuCu₂Si₂ 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 showed²,⁴,⁶–¹¹,¹⁷ that the effective valence of Eu in EuCu₂Si₂ changes from ~2.9 at 4.2 K, to ~2.6 at 300 K, and to ~2.3 at 500 K. The ternary compound EuCu₂Si₂ shows no magnetic ordering down to 0.4 K.² All the experimental studies mentioned above were carried out on EuCu₂Si₂ in a polycrystalline form.

Recently, single crystals of EuCu₂Si₂ were synthesized¹⁸,¹⁹ for the first time via an In flux method.²⁰ Astonishingly, magnetic susceptibility, electron spin resonance, and specific-heat data¹⁸,¹⁹ 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 ¹⁵¹Eu Mössbauer spectroscopy (MS) investigations of single crystals of EuCu₂Si₂. 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 EuCu₂Si₂ compounds.

II. EXPERIMENTAL METHODS

Single crystals of EuCu₂Si₂ 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 1:1.5 ratio with In flux, and sealed into an evacuated quartz tube. The crystals were synthesized by heating to 1150 °C at a rate of 30 °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 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 dc and ac magnetic susceptibilities were measured on ground single crystals using a Quantum Design magnetic property measurement system (MPMS-XL.7). 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 ¹⁵¹Eu Mössbauer measurements were conducted using a standard, constant acceleration Mössbauer spectrometer operating in sine mode and a ¹⁵¹Sm(SmF₃) 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 foil²¹ 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/cm².

The Mössbauer source ¹⁵¹Sm(SmF₃) used is not a monochromatic source as ¹⁵¹Sm nuclei are located in the SmF₃ matrix at a site of noncubic symmetry. By measuring the ¹⁵¹Eu Mössbauer spectra of a cubic EuSe compound we determined²² that the electric quadrupole coupling constant eQgVzz (Ref. 23) in our source is ~3.69(13) mm/s [Qg =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 ¹⁵¹Eu Mössbauer spectra. The isomer shift δ of the ¹⁵¹Eu Mössbauer spectra is given here relative to the ¹⁵¹Sm(SmF₃) source at room temperature.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Structural characterization

The ternary compound EuCu₂Si₂ crystallizes in the ThCr₂Si₂-type crystal structure²⁶ with the tetragonal space group I4/mmm (No. 139). There are 2 formula units of

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EuCu2Si2 per unit cell. The room-temperature x-ray powder-diffraction pattern of EuCu2Si2 is shown in Fig. 1. Table I lists the structural parameters of EuCu2Si2 obtained from the Rietveld refinement\textsuperscript{27} of the spectrum in Fig. 1.

The EuCu2Si2 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 EuCu2Si2 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 $\chi^2$ 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.\textsuperscript{18,19}

B. Magnetic susceptibility

The temperature dependence of the magnetic susceptibility $\chi$ of EuCu2Si2 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

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

where $\chi_0$ is the temperature-independent magnetic susceptibility, $C$ is the Curie constant, and $\Theta_p$ 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, $\mu_{eff}$ is the effective magnetic moment, and $k_B$ is the Boltz-
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magnetic susceptibility of EuCu$_2$Si$_2$ for selected frequencies 22.44 mK and field-cooled moments ordered antiferromagnetically below 10.6 K. 

The occurrence of a bifurcation between the ZFC and FC data is evident. This proves that the studied compound is a spin glass. 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. 

The temperature dependence of the real part $\chi'$ of the ac magnetic susceptibility of EuCu$_2$Si$_2$ 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. 

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

$$K = \frac{\Delta T_f}{T_f \Delta \log f}.$$ 

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-
The frequency-dependent maximum of $\chi'(T)$ indicates the freezing temperature $T_f$, where the maximum relaxation time, $\tau$, 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 $\tau \sim T^{-z}$, where $z$ is the correlation length and $\nu$ is the critical correlation-length exponent.\cite{29,30} Therefore, the temperature dependence of $f$ obeys the power-law divergence\cite{29,30}

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

(3)

where $f_0$ is the microscopic relaxation time. The best fit of the $T_A(f)$ data to Eq. (3) (Fig. 6) gives $f_0=2.57(29) \times 10^{11}$ Hz, $T_{SG}=11.74(13)$ K, and $\nu=5.26(80)$. The derived values of $f_0$ and $\nu$ are similar to those found for many different spin glasses.\cite{29,31}

C. Mössbauer spectroscopy

The $^{151}$Eu Mössbauer spectra of EuCu$_2$Si$_2$ recorded at temperatures at which no magnetic dipole hyperfine interaction\cite{23} is present are shown in Fig. 7. In contrast to the Mössbauer spectra of polycrystalline EuCu$_2$Si$_2$ (Refs. 1, 8, and 12), the spectra of the studied single-crystal specimen consist of one line located at $\delta=-8.7$ mm/s. This proves that Eu is divalent\cite{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.\cite{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\cite{23} and the resonance line shape of the spectra was described using a transmission integral formula.\cite{33}

The electric quadrupole coupling constant $eQgV_{zz}$ 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 $3.10(15) \times 10^{-2}$ mm/s/K. The absorption area $A(T)$ of a Mössbauer spectrum is proportional to the absorber Debye-Waller factor $f_a$ given\cite{23} by

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

(4)

where $M$ is the mass of the Mössbauer nucleus, $c$ is the speed of light, $E_\gamma$ is the energy of the Mössbauer transition, and $\Theta_D$ 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 $\Theta_D$ is close to the value of 210 K found from the specific heat data for polycrystalline EuCu$_2$Si$_2$.\cite{2}

Figure 9 shows the $^{151}$Eu Mössbauer spectra of EuCu$_2$Si$_2$ 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 $\delta=-8.6$ mm/s. This conclusively proves that Eu is
EuCu$_2$Si$_2$ obtained at the indicated temperatures, fitted
spectively.

The solid line is the fit to Eq. (4), as explained in the text.

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,$^{33}$ are 403.2(1.1) kOe,
6.710(202) mm/s and 386.4(1.2) kOe, 6.822(197) mm/s, re-
spectively.

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 $H_{hf}$. 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 elec-
tric field gradient principal axis with frequencies $f_+$ and $f_-.$

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 param-
eters were $f$ and $m$ (or equivalently $f_+$ and $f_-,$ $eQ_gV_{zz}, \delta,$ and total absorption (the linewidth was fixed to the value ob-
tained from the fit of the 4.4 K spectrum). As can be seen in
Fig. 9, the uniaxial relaxation model reproduces the experi-
mental relaxation spectra of EuCu$_2$Si$_2$ 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.$^{28,37}$ The inequality $T_f^M > T_{SG}$ results from the time window $\tau_{exp}$ of the experimental technique used to determine the freezing temperature. For MS, $\tau_{exp}$ is given by the Larmor precession time $\tau_L = \omega_l^{-1} = \mu_l B_{exp}$, where $\omega_l$ is the angular Larmor frequency, and $\mu_l$ and $B_{exp}$ 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 $\tau$ of fluctu-

![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.](image)

![FIG. 9. (Color online) The $^{151}$Eu Mössbauer spectra of EuCu$_2$Si$_2$ 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.](image)

![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.](image)
ating spin clusters in a spin glass,\textsuperscript{29,37,39} those clusters fluctuating with $\tau$ larger than $\tau_{\text{exp}}$ 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 $\tau_{\text{exp}}$. Thus, one expects to observe an increase of $T_{SG}$ with decreasing $\tau_{\text{exp}}$, which is indeed universally observed in spin glasses.\textsuperscript{29,37}

It is rather intriguing to observe diametrically different physical properties of apparently single-phase polycrystalline\textsuperscript{1–17} and single-crystal\textsuperscript{18,19} samples of the EuCu$_2$Si$_2$ 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$_2$Si$_2$ 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$_2$Si$_2$ 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$_2$Si$_2$ is found to be 233(1) K.

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