

**Antiferromagnetic ordering of divalent Eu in  $\text{EuCu}_2\text{Si}_2$  single crystals**

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We report the synthesis, from an indium flux, of single crystals of  $\text{EuCu}_2\text{Si}_2$ . In contrast to previous studies of polycrystalline samples in which intermediate-valent behavior for Eu is reported, we find that in single crystals of  $\text{EuCu}_2\text{Si}_2$  the behavior of Eu is divalent, including the presence of antiferromagnetic order at 10 K. The origins of these variations in ground-state properties are discussed in terms of effective chemical pressure and local changes in chemical environment.

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**I. INTRODUCTION**

Europium, because it is near half filling in the lanthanide row, can exhibit intermediate-valence character in certain compounds.<sup>1</sup> In the intermediate-valence regime, the Eu ion fluctuates between  $4f^6$  ( $\text{Eu}^{3+}$ ) and  $4f^7$  ( $\text{Eu}^{2+}$ ) configurations. The effective valence that results from this interconfigurational fluctuation is a function of temperature, pressure, applied magnetic field, and local chemical environment. The response to these perturbations can be abrupt—a first-order change in effective valence—or gradual—due to an effective change in population of the integral valence states. The  $\text{ThCr}_2\text{Si}_2$  crystal structure has proven to be a particularly compliant host for such phenomena, with well-documented examples of both valence transitions<sup>2-4</sup> and stable intermediate-valence behavior<sup>5-8</sup> being reported.

$\text{EuCu}_2\text{Si}_2$  is both one of the first europium-based compounds in which intermediate-valence behavior was observed and one of the most well studied.<sup>5,6</sup> Previous Mössbauer and magnetic susceptibility studies find that the effective valence of Eu in  $\text{EuCu}_2\text{Si}_2$  evolves from  $\sim 2.6$  at room temperature to  $\sim 2.8$  at lowest temperature. Because  $\text{Eu}^{3+}$  is a nonmagnetic  $J=0$  configuration, the susceptibility of  $\text{EuCu}_2\text{Si}_2$  is found to be small and temperature independent. Consistent with this observation, Mössbauer studies find an absorption spectrum with a majority contribution due to  $\text{Eu}^{3+}$  and a minority contribution due to  $\text{Eu}^{2+}$ , with the relative admixture of the two evolving slowly and smoothly as a function of temperature. The energetics of this behavior have been modeled successfully using the interconfigurational fluctuation model.<sup>9</sup>

Recently, as part of a broader study of  $\text{ThCr}_2\text{Si}_2$ -based rare-earth intermetallics, we have synthesized single crystals of  $\text{EuCu}_2\text{Si}_2$  from an In flux. In striking contrast to the intermediate-valence behavior previously reported for  $\text{EuCu}_2\text{Si}_2$ , we observe local-moment susceptibility consistent

with fully divalent Eu and antiferromagnetic order at 10 K. Subsequent synthesis efforts reveal that the magnetic properties of  $\text{EuCu}_2\text{Si}_2$  depend strongly on the preparation techniques that are employed. In what follows, we discuss the properties of the  $\text{EuCu}_2\text{Si}_2$  samples that we have prepared and speculate as to the origin of the variability in Eu valence that is observed.

**II. EXPERIMENTAL AND SAMPLE DETAILS**

Data are presented for single crystals of  $\text{EuCu}_2\text{Si}_2$  grown from an indium flux and for polycrystalline samples prepared in a sealed tantalum tube, a technique similar to arc melting, the synthetic method of choice in previous studies of  $\text{EuCu}_2\text{Si}_2$ . The single crystals were prepared by combining stoichiometric ratios of high-purity ( $>99.99\%$ ) Eu, Cu, and Si in a 1:20 ratio with In. The material was placed in an alumina crucible, sealed in an evacuated quartz ampoule, heated to 1150 °C, and then slow-cooled at a rate of 10 °C/h to 650 °C, at which point the grown crystals were decanted from the flux using a centrifuge. The resulting crystals presented a well-faceted rectangular-parallelepiped morphology with typical dimensions  $2 \times 2 \times 1 \text{ mm}^3$ .

Polycrystalline material was prepared by sealing stoichiometric ratios of the same high-purity starting materials of Eu, Cu, and Si in a tantalum tube. Such tubes were placed in an inert atmosphere and subjected to a variety of heating and annealing cycles. The enclosed environment of the sealed tube minimizes evaporative losses of Eu, which is very volatile at high temperature, and allows for more controlled sample melting than does direct argon arc melting. The particular samples discussed below were prepared as follows. Sample poly#1 was prepared by heating the material to 1350 °C for 10 min followed by a fast cooling to room temperature. For poly#2, the sample was heated to 1250 °C, held at this temperature for 12 h, and subsequently annealed at

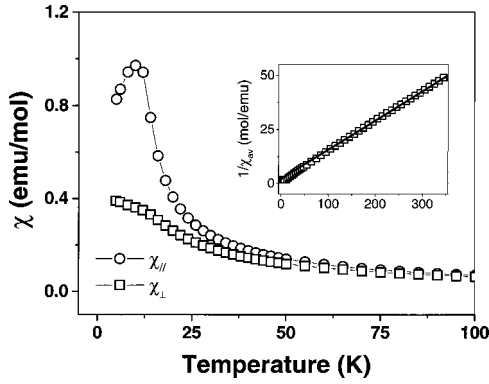


FIG. 1. Magnetic susceptibility of single-crystal  $\text{EuCu}_2\text{Si}_2$ . The data were obtained using a 1-kOe field applied parallel (circles) and perpendicular (squares) to the crystallographic  $c$  axis. The inset shows inverse susceptibility versus temperature for the polycrystalline average of these data.

850 °C for 7 days. Although a clear variation in effective valence could be produced (see below), we were unable to demonstrate a one-to-one correspondence between any particular detail of the preparation cycle (many additional thermal cycles were attempted in addition to those discussed explicitly here) and the effective valence of the samples.

The resulting samples were characterized by x-ray powder diffraction. The flux-grown single crystals were found to be single phase, crystallizing in the tetragonal  $\text{ThCr}_2\text{Si}_2$  structure with lattice constants  $a=4.111$  Å and  $c=9.968$  Å. For the polycrystalline samples, the lattice constants were found to depend on the details of the preparation (poly#1:  $a=4.08$  Å,  $c=9.96$  Å; poly#2:  $a=4.05$  Å,  $c=9.96$  Å). A small, unidentified second phase was found in some polycrystalline samples, which also gave rise to a ferromagnetic signal in susceptibility at  $\sim 100$  K.

Diagnostics of europium valence that we employed were the effective magnetic moment obtained from the high- $T$  magnetic susceptibility data, the magnetic entropy recovered at 20 K and electron-spin-resonance (ESR) measurements. Magnetic susceptibility was measured using a Quantum Design superconducting quantum interference device magnetometer. ESR measurements were carried out at X band in a conventional Bruker ESR spectrometer using a  $\text{TE}_{102}$  room-temperature cavity. The sample temperature was varied using a helium gas-flux temperature controller. Additionally, heat capacity and electrical resistivity measurements (using standard thermal relaxation and four-wire ac-excitation techniques, respectively) were performed on the single-crystal samples.

### III. RESULTS

#### A. Single crystals

In Fig. 1 we show the temperature dependence of the magnetic susceptibility, for an applied field  $H$  along the  $c$  axis  $\chi_{||}$  in the  $ab$  plane  $\chi_{\perp}$  and the polycrystalline average of the data  $\chi_{\text{av}}$  for single-crystal  $\text{EuCu}_2\text{Si}_2$ . The high-temperature data have a clear Curie-Weiss temperature dependence. For  $T > 150$  K, fits to the inverse susceptibility

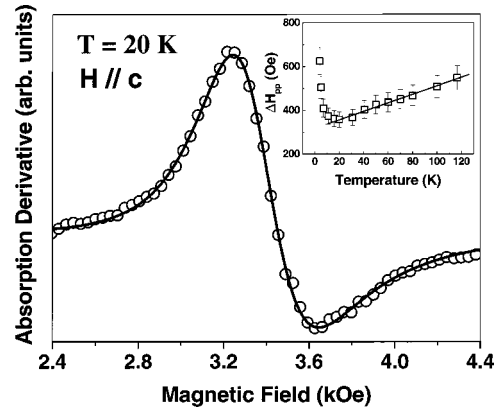


FIG. 2. ESR spectrum for single-crystal  $\text{EuCu}_2\text{Si}_2$ . The inset shows the temperature evolution of the fitted linewidth.

using polycrystalline average of these data (see inset), yield an effective moment of  $7.8(1)\mu_B$  and a paramagnetic Weiss temperature of  $-18(2)$  K. These data are entirely consistent with the magnetic behavior expected for divalent Eu—the free-ion effective moment for  $\text{Eu}^{2+}$  is  $7.94\mu_B$ . A clear signature of antiferromagnetic order is observed at 10 K. This ordering temperature is comparable to that of  $\text{EuCu}_2\text{Ge}_2$  (13 K) in which divalent Eu behavior has been clearly established,<sup>10</sup> and  $\text{GdCu}_2\text{Si}_2$  (11.9 K).<sup>11</sup>

ESR measurements on single crystals of  $\text{EuCu}_2\text{Si}_2$  present a single resonance with Landé  $g$  factor  $g \sim 2$  and confirm magnetic order at  $\sim 10$  K. Figure 2 shows the observed ESR spectrum for an applied field  $H$  along the  $c$  axis at 20 K. A typical Dysonian line shape [ $A/B \sim 2.2(2)$ ] is observed. This line shape is characteristic of localized magnetic moments in a metallic host with a skin depth smaller than the size of the sample particles.<sup>12</sup> The  $g$  value and linewidth  $\Delta H$  were obtained by fitting the resonance to the appropriate admixture of absorption and dispersion.<sup>13</sup> The solid line in Fig. 2 is the best fit to the observed resonance and gives  $g = 2.003(2)$  and  $\Delta = 360(40)$  Oe. The  $g$  value is slightly anisotropic, with  $g_{||} = 2.003(5)$  and  $g_{\perp} = 1.997(5)$ . Polycrystalline average of data for the temperature dependence of the peak-to-peak linewidth for  $\text{EuCu}_2\text{Si}_2$  single crystals is plotted in the inset of Fig. 2. The high- $T$  linear dependence (Korringa-rate)<sup>14</sup> indicates that the spin-relaxation process is mainly given by the interaction between the localized  $4f$  electron and the conduction electrons. The broadening of the ESR resonance linewidth for  $T \leq 10$  K is also a signature of magnetic order below 10 K. The obtained  $g_{\text{av}} = 2.001(3)$  and the small Korringa-rate ( $1-2$  Oe/K) for our  $\text{EuCu}_2\text{Si}_2$  single crystals are in good agreement with reported ESR data in  $\text{GdCu}_2\text{Si}_2$  in which again a single resonance was observed [ $g = 2.00(1)$ ,  $\Delta H/\Delta T \leq 0.5$  Oe/K].<sup>15</sup> This result strongly suggests that the observed resonance in our  $\text{EuCu}_2\text{Si}_2$  single crystals arises from the  $\text{Eu}^{2+}$  ions, which has the same  $4f^7$  ( $J = \frac{7}{2}$ ,  $L = 0 \rightarrow g \sim 2$ ) electronic configuration of  $\text{Gd}^{3+}$ . However, due to the high sensitivity ( $< 0.01\%$ ) of the ESR technique to any paramagnetic impurity in the sample, ESR studies in  $\text{LaCu}_2\text{Si}_2$  prepared in the same way as our  $\text{EuCu}_2\text{Si}_2$  single crystals would be valuable to confirm this statement.

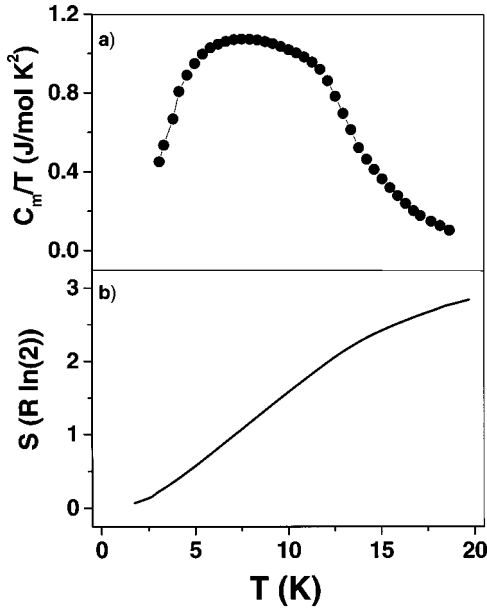


FIG. 3. Magnetic heat capacity divided by temperature (a) and magnetic entropy (b) of single-crystal  $\text{EuCu}_2\text{Si}_2$ . The phonon contribution for total heat capacity of  $\text{EuCu}_2\text{Si}_2$  was estimated from the specific-heat data of  $\text{LaCu}_2\text{Si}_2$  (Ref. 11).

Heat-capacity measurements confirm the long-range-ordered magnetic ground state of  $\text{EuCu}_2\text{Si}_2$ . Figure 3 shows the magnetic heat capacity divided by temperature and the corresponding magnetic entropy [Figs. 3(a) and (b), respectively] plotted versus temperature for  $\text{EuCu}_2\text{Si}_2$ . Although at first glance the magnetic transition may not be obvious, these data are entirely analogous to heat capacity for similar Gd-based antiferromagnets and magnetic Eu-based compounds, for which the broad character of the heat-capacity anomaly has been attributed to peculiarities in the exchange interaction in the ordered state<sup>11</sup> and to the presence of small crystal-field splitting,<sup>16</sup> respectively. Divalent Eu is expected to present similar magnetic properties of Gd-based materials, again because both ions are in a  $4f^7$  ( $J = \frac{7}{2}$ ) configuration. The recovered magnetic entropy at 20 K is closed to  $3 \ln 2$  which is the value expected for  $J = \frac{7}{2}$ . Electrical resistivity measurements for  $\text{EuCu}_2\text{Si}_2$  are shown in Fig. 4. The tem-

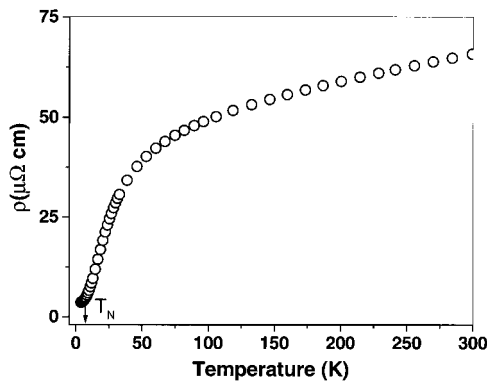


FIG. 4. Electrical resistivity versus temperature for single-crystal  $\text{EuCu}_2\text{Si}_2$ .

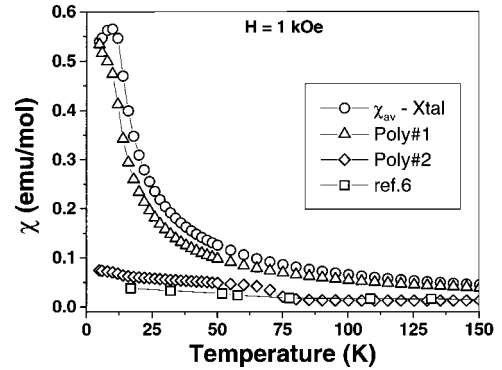


FIG. 5. Magnetic susceptibility for several samples of  $\text{EuCu}_2\text{Si}_2$ . The circles correspond to the polycrystalline average of the single-crystal data of Fig. 1. The squares are after Ref. 6. See text for sample preparation details for poly#1 (triangles) and poly#2 (diamonds).

perature dependence of the resistivity is typical of a good metal [ $R(T=300\text{ K})/R(T=5\text{ K}) = 17$ ], and the residual resistivity [ $\rho(5\text{ K}) = 4\ \mu\Omega\text{ cm}$ ] is quite small. Taken together, these data argue against gross disorder as the origin of the divalent behavior of Eu.

### B. Polycrystalline samples

Given the striking difference in behavior that we observe in single crystals compared to previously reported arc-melted samples, we were prompted to prepare polycrystalline samples of our own. We should point out, however, quite explicitly that it is not our belief that previous samples were somehow “low quality.” Rather, we believe that intrinsic crystal-chemical subtleties exist that produce the diverse range of behaviors that are observed. It is clear that a range of effective valences exist among our samples at room temperature. Because the ionic radius of divalent Eu is substantially larger than trivalent Eu, the observed decrease in unit-cell volume ( $V_{\text{crystal}} = 168.5\ \text{\AA}$ ,  $V_{\text{poly\#1}} = 165.8\ \text{\AA}$ ,  $V_{\text{poly\#2}} = 163.4\ \text{\AA}$ ) is consistent with increasingly trivalent Eu. This observation is confirmed by the magnetic susceptibility data of Fig. 5. In addition to data from our two polycrystalline samples, we show the data of Sales and Viswanathan for arc-melted  $\text{EuCu}_2\text{Si}_2$ ,<sup>6</sup> as well as repeat the single-crystal data of Fig. 1. Again, because trivalent Eu is in a nonmagnetic configuration, decreasing low-temperature susceptibility is consistent with increasingly trivalent Eu.

## IV. DISCUSSION

Given the substantial evidence both for divalent Eu in our single crystals and for nearly trivalent Eu in previous reports, the question of interest is not which report is correct, but rather how  $\text{EuCu}_2\text{Si}_2$  can display such diverse properties as a function of preparation method. In fact, hints that  $\text{EuCu}_2\text{Si}_2$  might exist in a divalent configuration already exist in the literature. Previous Mössbauer studies of  $\text{EuCu}_2\text{Si}_2$  consistently report the existence of an “impurity” contribution due to purely divalent Eu in addition to the primary intermediate valence spectrum.<sup>5,17</sup> This impurity signal has been ascribed

not to a secondary phase within the sample but rather to a particular defect structure in  $\text{EuCu}_2\text{Si}_2$ .<sup>5</sup> On the other hand, doping studies performed on  $\text{EuCu}_2\text{Si}_2$  (e.g.,  $\text{EuCu}_2\text{Si}_{2-x}\text{Ge}_x$  and  $\text{EuCu}_{2+x}\text{Si}_{2-x}$ ) clearly reveal the stabilization of a divalent, magnetically ordered phase.<sup>17</sup> Although local chemical effects have also been suggested here (due, for example, to a multiplicity of locally inequivalent Eu sites<sup>17</sup>), a negative effective chemical pressure appears to be the simplest origin of this behavior.

To test this simple hypothesis we have performed magnetic susceptibility measurements on single-crystal  $\text{EuCu}_2\text{Si}_2$  as a function of pressure. The pressure cell that we employed for these experiments is limited to 5 kbars. At these pressures, no shift in the Néel temperature is observed, and only a weak ( $\sim 5\%$ ) decrease in 5-K susceptibility is found. To put this result in context,  $\text{EuCu}_2\text{Si}_{1.5}\text{Ge}_{0.5}$  is reported to have a unit-cell volume of  $172.3 \text{ \AA}^3$  and  $T_N = 12 \text{ K}$ .<sup>17</sup> Our single crystals have a unit-cell volume of  $168.5 \text{ \AA}^3$  and  $T_N = 10 \text{ K}$ . Thus if chemical pressure were the only effect of doping and assuming a linear relationship between cell volume and  $T_N$ , at 5 kbars we should observe  $T_N = 9.5 \text{ K}$  [the bulk modulus of  $\text{EuCu}_2\text{Si}_2$  is 1 Mbar (Ref. 18)], which is inconsistent with our data ( $\Delta T_N < 0.1 \text{ K}$ ). A comparison of the local crystallographic structure of our single-crystal and polycrystalline samples of  $\text{EuCu}_2\text{Si}_2$  would be valuable in identifying the type(s) of local distortion that stabilize diva-

lent Eu.<sup>19</sup> Additionally, the fact that  $T_N$  appears to be pressure independent at low pressure might suggest the proximity of a pressure-induced first-order valence transition; however, measurements to higher pressure are clearly required to test this speculation.

## V. CONCLUSIONS

We have reported the growth of  $\text{EuCu}_2\text{Si}_2$  single crystals from an In flux. Rather than the expected intermediate-valence behavior previously reported for  $\text{EuCu}_2\text{Si}_2$ , we observe properties that are consistent with a divalent configuration for Eu, including the observation of antiferromagnetic order at 10 K. Our preliminary pressure experiments suggest that the divalent configuration of Eu found in single crystals is not solely an effect of negative chemical pressure but rather is a consequence of variations in local crystal chemistry that result from the particular synthetic approach that is employed. In this regard,  $\text{EuCu}_2\text{Si}_2$  is reminiscent of its structural relative  $\text{CeCu}_2\text{Si}_2$ .<sup>20</sup>

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- <sup>1</sup>I. Nowik, *Hyperfine Interact.* **13**, 89 (1983).  
<sup>2</sup>A. Mitsuda, H. Wada, M. Shiga, H. Aruga Katori, and T. Goto, *Phys. Rev. B* **55**, 12 474 (1997).  
<sup>3</sup>M. Chefki, M. M. Abd-Elmeguid, H. Micklitz, C. Huhnt, W. Schablit, M. Reehuis, and W. Jeitschko, *Phys. Rev. Lett.* **80**, 802 (1998).  
<sup>4</sup>H. Wada, M. F. Hundley, R. Movshovich, and J. D. Thompson, *Phys. Rev. B* **59**, 1141 (1999).  
<sup>5</sup>E. R. Bauminger, D. Froindlich, I. Nowik, S. Ofer, I. Felner, and I. Mayer, *Phys. Rev. Lett.* **30**, 1053 (1973).  
<sup>6</sup>B. C. Sales and R. Viswanathan, *J. Low Temp. Phys.* **23**, 449 (1976).  
<sup>7</sup>E. V. Sampathkumaran, L. C. Gupta, R. Vijayaraghavan, K. V. Gopalakrishnan, R. G. Pillay, and H. G. Devare, *J. Phys. C* **14**, L237 (1981).  
<sup>8</sup>M. M. Abd-Elmeguid, Ch. Sauer, and W. Zinn, *J. Phys. C* **18**, 345 (1985).  
<sup>9</sup>J. Rohler, D. Wollleben, G. Kaindl, and H. Balster, *Phys. Rev. Lett.* **49**, 65 (1982).  
<sup>10</sup>I. Felner and I. Nowik, *J. Phys. Chem. Solids* **39**, 767 (1978).  
<sup>11</sup>M. Bouvier, P. Lethuillier, and D. Schmitt, *Phys. Rev. B* **43**, 13 137 (1991); J. A. Blanco, D. Gignoux, and D. Schmitt, *ibid.* **43**, 13 145 (1991).  
<sup>12</sup>G. Feher and A. F. Kip, *Phys. Rev.* **98**, 337 (1953); F. J. Dyson, *ibid.* **98**, 349 (1955).  
<sup>13</sup>G. E. Pake and E. M. Purcell, *Phys. Rev.* **74**, 1184 (1948).  
<sup>14</sup>J. Korryng, *Physica (Amsterdam)* **16**, 601 (1950).  
<sup>15</sup>E. Kwapulinska, K. Kaczmarzka, and A. Szytula, *J. Magn. Magn. Mater.* **73**, 65 (1988).  
<sup>16</sup>S. Süllow, I. Prasad, M. C. Aronson, J. L. Sarrao, Z. Fisk, D. Hristova, A. H. Lacerda, M. F. Hundley, A. Vigliante, and D. Gibbs, *Phys. Rev. B* **57**, 5860 (1988).  
<sup>17</sup>I. Nowik, I. Felner, C. Mermelstein, and E. R. Bauminger, *Hyperfine Interact.* **54**, 847 (1990).  
<sup>18</sup>G. Neumann, J. Langen, H. Zahel, D. Plumacher, Z. Kletowski, W. Schlabitz, and D. Wohlleben, *Z. Phys. B: Condens. Matter* **59**, 133 (1985).  
<sup>19</sup>For such a study in the case of  $\text{CeCu}_2\text{Si}_2$ , see D. Louca, J. D. Thompson, J. M. Lawrence, R. Movshovich, C. Petrovic, J. L. Sarrao, and G. H. Kwei, *Phys. Rev. B* **61**, 14 940 (2000).  
<sup>20</sup>K. Ishida, Y. Kawasaki, K. Tabuchi, K. Kashima, Y. Kitaoka, K. Asayama, C. Geibel, and F. Steglich, *Phys. Rev. Lett.* **82**, 5353 (1999).