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2003 J. Phys.: Condens. Matter 15 3307

(http://iopscience.iop.org/0953-8984/15/19/329)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 3307–3313 PII: S0953-8984(03)59371-7

Antiferromagnetic transition in $EuCu_2Ge_2$ single crystals

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Received 10 February 2003
Published 6 May 2003

Abstract

Single crystals of $EuCu_2Ge_2$ were grown and characterized using electrical resistivity, magnetization, specific heat and magnetoresistance measurements. The crystals exhibit antiferromagnetic transitions at $T_{N1} = 9$ K and $T_{N2} = 5$ K. The T_N of the flux-grown single crystals reported here are lower than that reported for the polycrystalline sample ($T_N = 13$ K) in the literature (Felner and Nowik 1978 *J. Phys. Chem. Solids* **39** 763). The magnetoresistance is positive in the ordered state and negative in the paramagnetic state. The magnetic order could not be suppressed up to a pressure of 25 kbar.

1. Introduction

EuM_2X_2 (M = transition metal, X = Si, Ge) compounds have been reported to be in a stable divalent (magnetic) or trivalent (nonmagnetic) or a valence fluctuating state [2]. Polycrystalline $EuCu_2Si_2$ is a well known and thoroughly investigated valence fluctuating compound [3, 4]. In contrast to the well established valence fluctuating nature of the polycrystalline samples flux-grown single crystals of $EuCu_2Si_2$ were reported recently to show magnetic order at 10 K [5]. In this context, it is of interest to investigate the magnetic properties of the flux grown single crystals of the stable divalent compound $EuCu_2Ge_2$. Felner and Nowik [1] investigated polycrystalline $EuCu_2Ge_2$ using magnetic susceptibility and Mössbauer spectroscopy. They observed a peak in the magnetic susceptibility at 13 K and from the analysis of the hyperfine interaction they derived the angle between the hyperfine field and *c*-axis to be 52°. We present the resistivity, magnetic susceptibility, specific heat and magnetoresistance results for single crystals of $EuCu_2Ge_2$.

2. Experimental details

We have grown single crystals of $EuCu_2Ge_2$ using a molten In flux method, similar to the method employed for growing single crystals of $EuCu_2Si_2$ [5]. The single crystals formed

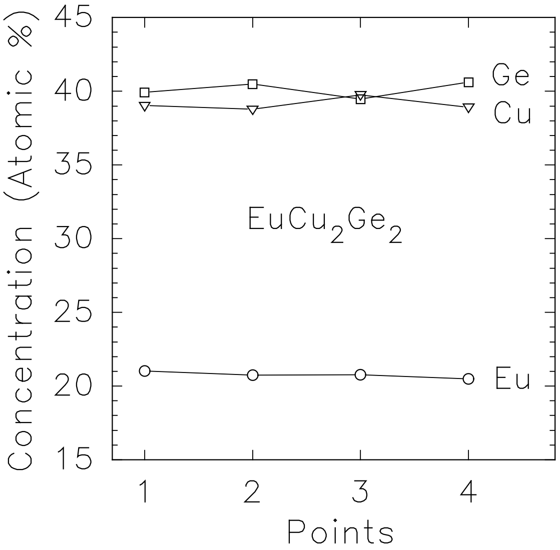

Figure 1. Atomic concentration of Eu, Cu and Ge obtained from EDXA.

as platelets with their *c*-axis perpendicular to the plane of the plate-like crystals. The single-crystalline nature was checked with the Laue method and the phase purity and lattice parameters were obtained using powder x-ray diffraction of crushed single crystals. The composition of the crystal was obtained using energy dispersive x-ray analysis (EDXA). Magnetization measurements were carried out using a commercial superconducting quantum interference device magnetometer. Resistivity, magnetoresistance and heat capacity measurements were carried out using ac transport and heat capacity options of a commercial physical property measurement system (Quantum Design).

3. Results and discussions

The single crystals form in a $ThCr_2Si_2$-type tetragonal structure with lattice parameters $a = 4.215$ Å and $c = 10.299$ Å. The lattice parameters are to be compared with $a = 4.215$ Å and $c = 10.18$ Å for the polycrystalline sample in [1]. The lattice volume of the flux-grown single crystal (182.974 Å^3) is 1.2% larger than that of the polycrystalline sample (180.860 Å^3). The relative volume change between flux-grown single crystal and the polycrystalline sample was even more (∼3%) in case of $EuCu_2Si_2$ [5]. The composition of $EuCu_2Ge_2$ crystal was found to be very close to 1:2:2 (figure 1).

The magnetic susceptibility (χ) data measured in a field of 0.1 T in the temperature range 5–300 K are shown in figure 2. The susceptibility is practically isotropic in the paramagnetic region as expected for an S-state ion in Eu^{2+} ($J = S = 7/2$). The data in the paramagnetic region follow Curie–Weiss behaviour in the temperature region 20–300 K with effective magnetic moment $\mu_{eff} = 8.0\ \mu_B$, Weiss temperature $\theta_P = -18.3$ K for $B \parallel c$ and $\mu_{eff} = 7.77\ \mu_B$, $\theta_P = -16.08$ K for $B \parallel (ab)$. The effective moment is very close to the value expected for divalent Eu^{2+} ions. These values are also close to $\mu_{eff} = 8.0\ \mu_B$ and $\theta_P = -20$ K reported for the polycrystalline sample in [1]. The θ_P values are only slightly larger in magnitude than T_N, suggesting negligible hybridization. The negative θ_P indicates the predominantly antiferromagnetic nature of the magnetic interaction which leads

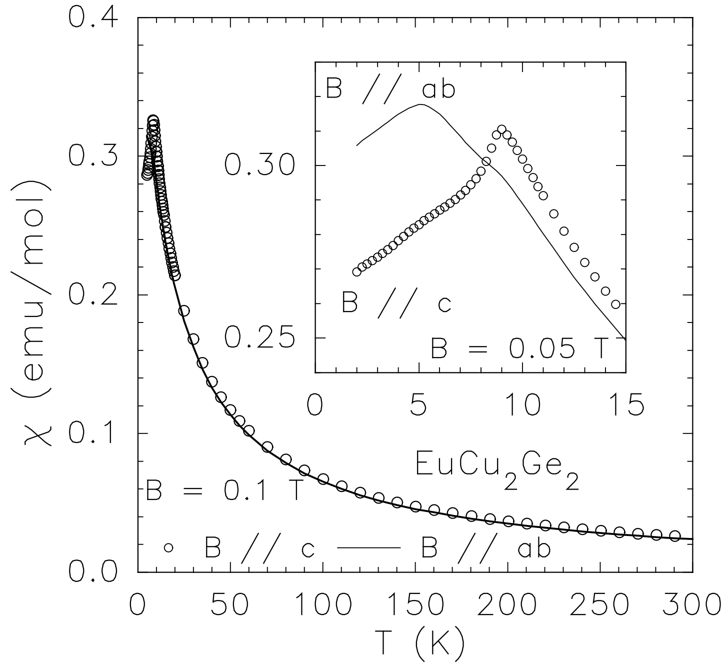

Figure 2. Magnetic susceptibility (χ) as a function of temperature for $EuCu_2Ge_2$ measured in a field of 0.1 T. The inset shows χ versus T at low temperatures.

to antiferromagnetic order at low temperature. The susceptibility data measured in a field of 0.05 T in the temperature range 2–15 K are shown in the inset to figure 2. For $B \parallel c$ χ exhibits a well defined peak at 9 K which is characteristic of an antiferromagnetic transition; a change of slope is also visible at 7 K. For $B \parallel (ab)$ there is a change of slope at 9 K and a well defined peak at 5 K. These χ data are a clear manifestation of the presence of two antiferromagnetic transitions at $T_{N1} = 9$ K and $T_{N2} = 5$ K in the single crystal of $EuCu_2Ge_2$. There is no significant difference between the susceptibility measured under zero-field-cooled and field-cooled conditions. The temperature dependence of χ for $B \parallel c$ and $B \parallel (ab)$ is consistent with the fact that the hyperfine field points in a direction 52° away from the c-axis [1]. In the magnetically ordered state magnetic moments lie neither along the c-axis nor in the (ab) plane.

The magnetization $M(B)$ measured at 2 K (ordered state) and 20 K (paramagnetic state) is shown in figure 3. The most interesting feature of the magnetization curves is the observation of a metamagnetic-like upward curvature for $B \parallel c$ at $T = 2$ K. The upward curvature is possibly due to some spin realignment. The transition is more clearly visible in the $\mathrm{d}M/\mathrm{d}B$ versus B curve (see inset to figure 3) as a peak at $B = 3.25$ T. The magnetization, however, does not show saturation up to 5 T. The magnetization at 2 K and 5 T for $B \parallel c$ corresponds to 2.5 μ_B/Eu which is much less than the saturation value of 7 μ_B for Eu^{2+}. Nearly linear behaviour of magnetization for the low-field region in the ordered state is consistent with the antiferromagnetic nature of the magnetic transition.

Figure 4 shows the specific heat C_p of $EuCu_2Ge_2$ together with that of the nonmagnetic compound $LaCu_2Ge_2$. Below 10 K, C_p of $LaCu_2Ge_2$ fits well with the expression $C_p = \gamma T + \beta T^3$. The linear coefficient of specific heat γ obtained from this fit is ~3 mJ mol^{-1} K^{-2} for $LaCu_2Ge_2$. The specific heat of $EuCu_2Ge_2$ shows a large anomaly ($C_{pmax} = 13$ J mol^{-1} K^{-1})

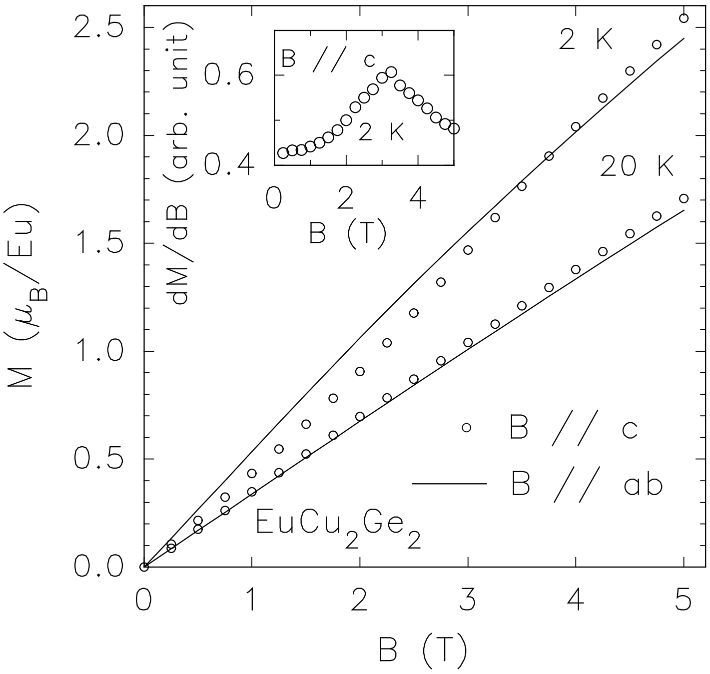

Figure 3. Magnetization as a function of magnetic field at 2 and 20 K.

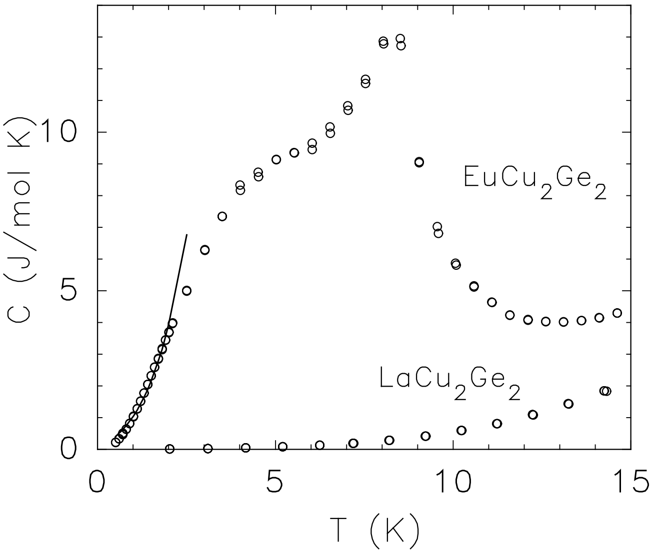

Figure 4. Specific heat of $EuCu_2Ge_2$ as a function of temperature. Prominent anomalies due to magnetic transitions are seen. The solid curve passing through the data points represents a fit to the expression mentioned in the text.

with a peak at 8.5 K which we associate with the first magnetic transition at T_{N1}. A further anomaly is observed at 5 K due to the second magnetic transition at T_{N2}. The magnetic susceptibility (figure 2 inset) and the resistivity data (figure 5 inset) also show anomalies

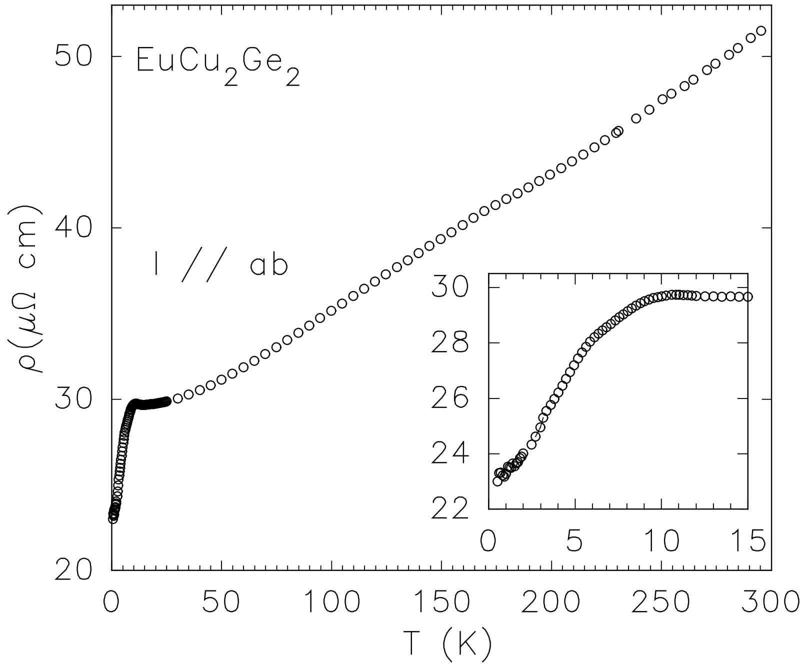

Figure 5. Electrical resistivity of EuCu$_2$Ge$_2$ in the temperature interval 0.5–300 K. The inset shows an expanded view in the low-temperature region.

at these temperatures. In the magnetically ordered state (below 2 K) the specific heat behaves as $\gamma_{AF}T + \beta_{AF}T^3$ with $\gamma_{AF} = 0.72$ J mol^{-1} K^{-2}. Considering that below 2 K the phonon contribution to the specific heat is negligible, the T^3 term is attributed mainly to the antiferromagnetic magnons. Since the magnetic entropy is $\sim 0.8R \ln 8$ at T_{N1} (9 K) and full entropy $R \ln 8$ corresponding to $J = 7/2$ for Eu^{2+} is attained at 20 K, we believe that the large γ value is mostly magnetic rather than electronic in origin. Hence, we do not classify EuCu$_2$Ge$_2$ as a heavy fermion antiferromagnet.

This interpretation is further supported by the simple metallic behaviour (figure 5) of the resistivity (ρ) of EuCu$_2$Ge$_2$ in contrast to the anomalous resistivity observed in heavy fermion/Kondo lattice antiferromagnets. ρ of EuCu$_2$Ge$_2$ at 300 K is 52 $\mu\Omega$ cm and the residual resistance ratio (RRR) is 2.3. At the same temperature ρ of LaCu$_2$Ge$_2$ is 26 $\mu\Omega$ cm (not shown). The much higher value of ρ for EuCu$_2$Ge$_2$ is a clear indication of strong spin disorder scattering of the charge carriers. At low temperature resistivity shows a mild maximum at 10 K below which the resistivity starts to decrease due to reduction in spin disorder scattering at T_{N1} (see figure 5 inset). A further decrease in the reduction of the spin disorder scattering is seen at T_{N2} by the visible change of slope.

The results of transverse magnetoresistance of EuCu$_2$Ge$_2$ are shown in figure 6. In the magnetically ordered state the magnetoresistance is positive (+5.3% at $T = 2$ K and $B = 6$ T). The magnetoresistance might be positive for an antiferromagnet due to the enhancement of the magnetic moment fluctuations in one of the two magnetic sublattices by the application of an external magnetic field [6]. In the paramagnetic state the magnetoresistance is negative (-1.4% at $T = 20$ K and $B = 6$ T). Though negative magnetoresistance in the paramagnetic region is more common in Kondo lattice/heavy fermion antiferromagnets due to freezing out of spin–flip scattering [7–9], it is also observed in other magnetic materials. As for an example,

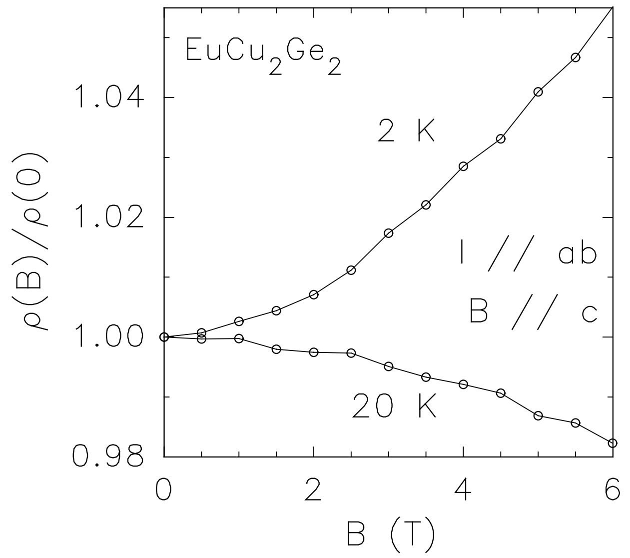

Figure 6. Normalized magnetoresistance at 2 and 20 K as a function of magnetic field.

the negative magnetoresistance in the paramagnetic region in $HoNi_2B_2C$ is attributed to the reduction of spin disorder scattering [10]. Since we do not find strong signatures of the Kondo effect in the resistivity data of $EuCu_2Ge_2$, we attribute the negative magnetoresistance in the paramagnetic region to the reduction of spin disorder scattering on application of an external magnetic field.

We wish to point out here that the magnetic ordering temperature of the single crystal is lower than that in the polycrystalline sample. Since the lattice volume of the flux-grown single crystal is larger than the polycrystalline sample, the magnetic transition temperature should increase initially up to a certain pressure, as was found in $EuNi_2Ge_2$ [11]. Eventually, sufficiently high pressure would suppress the magnetic transition and drive the system to the valence fluctuating state. Such studies would be rewarding, in particular to investigate whether the system undergoes a first-order transition from the magnetic to the valence fluctuating state as in the case of $EuNi_2Ge_2$ [11] or whether the system passes through a quantum critical point as in the case of $CePd_2Si_2$ or $CeIn_3$ [12]. Our preliminary investigation shows that the magnetic transition persists up to at least 25 kbar ($T_{N1} \sim 10$ K), as found by well defined anomaly in the resistivity data. Detailed investigation of the pressure response will be the subject of a future investigation.

4. Conclusions

The resistivity, magnetoresistance, magnetization and specific heat data provide conclusive evidence for the presence of successive magnetic transitions in $EuCu_2Ge_2$ at 9 and 5 K. The peak in the susceptibility with no difference between the zero-field-cooled and field-cooled values, linear behaviour of the magnetization in the low-field region and positive magnetoresistance in the ordered state are all consistent with the antiferromagnetic nature of the phase transition. Though the flux-grown crystals of $EuCu_2Ge_2$ have lower T_N than the polycrystalline sample, they do not show entirely different magnetic properties, as was found in valence fluctuating $EuCu_2Si_2$.

Acknowledgment

We would like to thank R Ramlau for the energy dispersive x-ray analysis.

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