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Magnetic phase transitions in intermetallic CeCuGe compound

Y. Oner[a,*], O. Kamer[a], Joseph H. Ross Jr[b], C.S. Lue[c], Y.K. Kuo[d]

[a]Department of Physics, Faculty of Sciences and Letters, Istanbul Technical University, Maslak, 34469 Istanbul, Turkey
[b]Department of Physics, Texas A&M University, College Station, TX 77843, USA
[c]Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan, ROC
[d]Department of Physics, National Dong Hwa University, Shou-Feng, Hualien 704, Taiwan, ROC

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Abstract

Electrical and magnetic properties of CeCuGe were investigated through electrical resistivity, thermal conductivity and magnetization measurements in the temperature range 2–300 K. Magnetization measurements indicate a paramagnetic to ferromagnetic transition at $T=10$ K, in agreement with previous work. There are two distinct paramagnetic regimes: At high-T the magnetic moment per cerium is 2.50 μ_B, nearly equal to the expected 2.54 μ_B for Ce^{3+}, while at low-T the effective moment decreases to 2.20 μ_B per cerium. This decrease is attributed to crystalline electric field effects. In the ferromagnetic region, the hysteresis curve indicates a rather small anisotropy (H_c less than 20 Oe). There is also very little remanence (the ratio of the remanence to the technical saturation magnetization is about 0.05), implying that this material is magnetically quite soft, with a very small magnetocrystalline anisotropy, contrary to what was reported in a previous investigation. In the temperature regime 10–30 K the resistivity obeys a T^2-behavior, consistent with the appearance of spin fluctuations above the ferromagnetic transition. In the same temperature regime, the thermo-power exhibits a linear rise in addition to a T^2 term, anomalous behavior which we also attribute tentatively to the development of spin fluctuations.

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1. Introduction

A substantial amount of experimental work has been performed to investigate the magnetic and electrical properties of ternary equiatomic lanthanide silicides and germanides with the general formula RTSi and RTGe (R = rare earth; T = transition metal), exhibiting several crystal structures [1]. The competition between exchange interactions and crystal field splitting gives rise to complex magnetic structures and to unusual magnetization processes. Despite a fairly large number of studies done on these compounds, there are still open questions to be considered. Of these, some Ce-based ternary compounds being stable under normal conditions can be driven to an unstable state by the application of hydrostatic pressure or a magnetic field. This is due to hybridization of the localized 4f electrons with the conduction electrons and a high density of states near the Fermi energy [2].

The hexagonal AlB_2-type compound CeCuGe has been earlier reported to be ferromagnetic at $T_c=10$ K [3]. Along with the closely related CeAuGe, it is thus one of the few Ce-based intermetallics to exhibit ferromagnetism [4,5]. The metallic behavior comes despite an 18 valence-electron count per formula unit (assuming magnetic Ce retaining a

* Corresponding author. Tel.: +90 212 285 32 60; fax: +90 212 285 63 86.
E-mail address: oner@itu.edu.tr (Y. Oner).

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single f electron) which acts as a strong stabilizer for certain intermetallic structures, yielding semiconducting behavior [6,7]. In this study, we have undertaken to measure the electrical resistivity, thermal conductivity and thermopower, together with the magnetization on CeCuGe in order to further elucidate the electrical and magnetic properties. The magnetic measurements confirm the dominance of Ce^{3+} in the high-temperature magnetic properties, while an observed reduction in the effective moment at lower temperatures is consistent with a crystal-field-induced splitting. However, just above T_c the appearance of a distinct T^2 behavior for the resistivity, as well as a non-standard temperature-dependence to the thermopower in the same temperature region, points to an additional contribution due to spin fluctuations in this material.

2. Experimental

Samples of CeCuGe were prepared for this study by arc melting the elemental constituents under argon atmosphere, using starting materials of 99.9% purity. The ingot was remelted several times. To ensure a homogeneous final material, the sample was annealed at 800 °C for 2 months. The structure was analyzed by X-ray diffraction using Cu K_α radiation. The sample was found to be single phase with a best structural fit obtained using the AlB_2 structure (space group designation *P6/mmm*, #191) as reported by Iandelli [8]. An alternative structure reported for this compound is the $InNi_2$ structure [3,9], which differs in the ordering of sublattice atoms. However, refinement indicated a best fit using the AlB_2 structure for our material. (Note that the magnetic T_c shown below is identical to what was reported in Ref. [3], making it unlikely that there is a real structural difference.) Lattice constants from the X-ray fit were found to be $a=4.316$ Å, and $c=3.967$ Å, in good agreement with what has been reported in the literature.

A SQUID magnetometer was used to measure the DC magnetization in the temperature range of 5–300 K in the presence of magnetic fields up to 55 kOe. The magnetic field was applied along the long side of the sample in order to minimize the demagnetization field. AC susceptibility measurements were performed using a commercial LakeShore AC susceptometer ($f=133.3$ Hz, $H=1$ mT) in the temperature range of 4–300 K.

Resistivity of the samples was measured with a standard DC four-probe set-up over a 4–300 K temperature range. A calibrated Ge thermometer (GR-200A-2500) was used to measure the temperature below 80 K. For higher temperatures, a calibrated Pt thermometer was used. Electrical contacts were made using silver paint and 25 μm gold wire.

The thermal conductivity study was carried out in a closed-cycle refrigerator over the temperature range from 10 to 300 K, using a direct heat-pulse technique. The CeCuGe ingot was cut to a rectangular parallelepiped shape of typical size $1.5\times1.5\times5.0$ mm^3 for the thermal conductivity (κ) and thermoelectric power (TEP) measurements. All experiments were performed while warming, at a rate slower than 20 K/h. The reproducibility of the measurements of κ and TEP was better than 2%, while the absolute accuracy of the κ measurements is approximately 15%, with the error mainly a result of the uncertainty in the measured sample geometry, and the heat loss. More details about the technique and measurements were given in [10].

3. Results and discussion

3.1. Magnetic measurements

Fig. 1 presents the temperature dependence of the magnetic susceptibility for CeCuGe in the temperature range 4–300 K, for an applied field of 20 Oe. The salient feature of the data is the sharp increase in the magnetization at the Curie temperature, $T_c=10$ K. As noted above, the T_c is identical to what has been reported previously [3]. From a plot of $1/M$ versus T (Fig. 2) it is also clear that above T_c the paramagnetic state separates into two regimes having different Curie-type behavior; a high-T regime between 53 K and room temperature, and a low-T regime in the temperature range 10–53 K. Both of the paramagnetic regimes follow a Curie–Weiss behavior, which allowed us to determine the effective paramagnetic moments per formula unit and the Curie temperatures. These are: $P_{eff}=2.50\ \mu_B$ and $\Theta_P=4.56$ K for the high-T regime and $P_{eff}=2.20\ \mu_B$ and $\Theta_P=10.2$ K for the low-T regime. Parameters for the low-T regime are also indicated on the inset of Fig. 1, where the fitted curve is shown. The temperature independent component, χ_0, which includes contributions due to the conduction electron Pauli magnetism and Landau

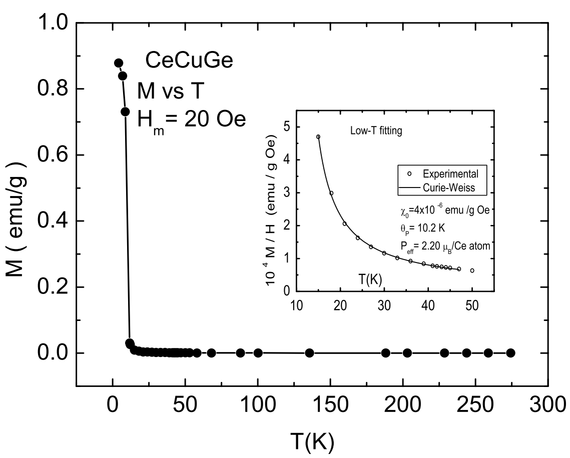

Fig. 1. Low-field magnetization (M) for CeCuGe versus T. The inset shows M/H versus T in the temperature range 15–50 K, together with the Curie–Weiss fit (the solid curve), and the parameters obtained from this fit.

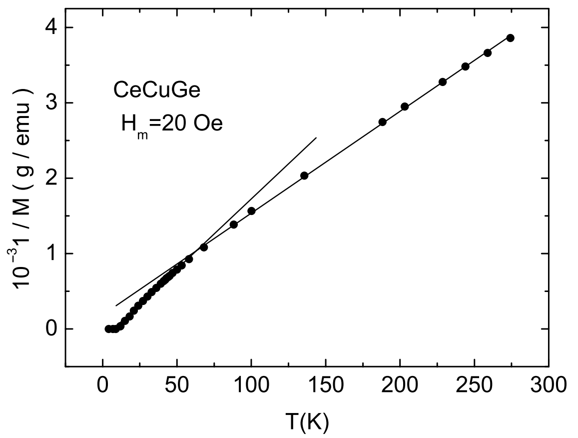

Fig. 2. 1/M versus T, with a measuring field $H_m = 20$ Oe. Note the slope change at about 53 K, indictating a crystal field effect on the magnetization.

diamagnetism, as well as the core diamagnetism, was found to be 3–4$\times 10^{-6}$ emu/g Oe for both regimes.

In the high-T regime, assuming that only Ce carries a localized moment, the effective moment of 2.50 μ_B per Ce is very close to that of the free Ce^{+3} ion (2.54 μ_B per atom). This implies that the Ce atoms carry fixed moments which dominate the high-T magnetic behavior of this material. In the low-T regime, the observed P_{eff} per Ce is as much as 0.34 μ_B less than the free ion value. The simplest explanation would be a crystal field effect, in which the crystal field splitting causes a subset of the Ce magnetic levels to freeze out at this temperature. Indeed, within the framework of the ionic model, the ground-state multiplet of a cerium atom ($4f^1$ configuration) corresponds to $J=5/2$ ($L=3$, $S=1/2$). In a crystal field (CF) of hexagonal symmetry, as in the present case, the $J=5/2$ level will be split into three doublets, each with a defined J_z value: $J_z = \pm 1/2$, $\pm 3/2$, and $\pm 5/2$. (Here we consider the ground-state multiplet alone, while the spin-orbit splitting, which is much larger than the CF effect, is omitted.) Therefore, one can ascribe this reduction in the magnetic moment to crystal-field-split states.

In the ferromagnetic regime, an M versus H plot obtained at 3 K for the range ± 5 kOe, shown in Fig. 3, demonstrates the magnetic hysteresis. The magnetization reaches its technical saturation value of about 1 μ_B within ± 2 kOe. It is to be noted that no demagnetization correction was done for these data. The extrapolation of M versus $1/H$ to $H=0$ yields approximately 1.2 μ_B, which corresponds to the expected magnetic moment for a Ce atom in the $J_z = 3/2$ doublet. We, therefore, suggest that the localized Ce atoms have been populated in the $J_z = 3/2$ levels below T_c. The hysteresis curve has exceedingly small anisotropy (H_c is less than 20 Oe). There is no remarkable remanent magnetization as well (the ratio of the remanent magnetization to the technical saturation magnetization value is about 0.05), implying very small magnetocrystalline anisotropy, contrary to what was previously reported [3].

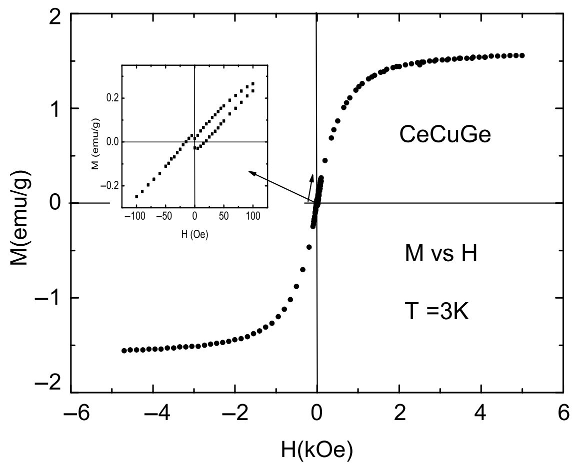

Fig. 3. Magnetization versus field at 3 K for CeCuGe. No sizable change was detected between zero field and field cooled cases. Note that the coercivities are very small. The inset shows data for low fields, from which the coercivity can be deduced to be about 20 Oe.

3.2. Electrical resistivity

In Fig. 4 we show the temperature dependence of the electrical resistivity of CeCuGe below room temperature. Like typical metals, $\rho(T)$ decreases almost linearly with decreasing temperature down to about 100 K. Below 100 K there is a gradual change to a temperature dependence rather close to T^2, while at 10 K there is a small but sharp drop corresponding to the ferromagnetic T_c. These data are quite similar in overall shape and magnitude to the data displayed previously in Ref. [9].

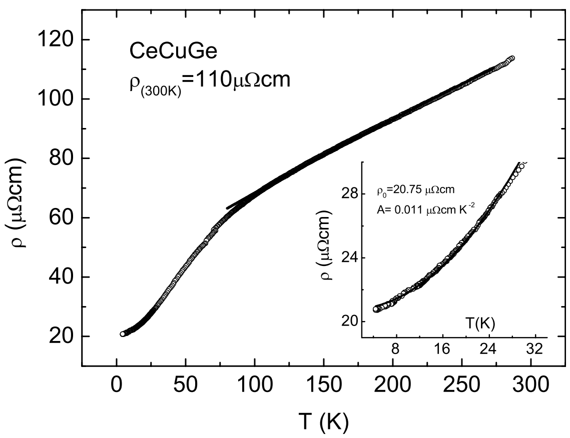

Fig. 4. CeCuGe resistivity as a function of temperature. The solid curve in the main plot is a fit to the Bloch–Grüneisen theory, as described in the text. Inset shows the low temperature data, and the fit to T^2 behavior over the range 10–30 K (solid curve in inset plot).

To describe the temperature dependence of the electrical resistivity, the high temperature data were fitted to the Bloch and Grüneisen (BG) expression, commonly used to describe the phonon-dominated regime in intermetallic compounds [11]. A fit to the BG expression over the temperature range 85–270 K yielded a Debye temperature of 240 K, with the fitted curve shown in the main plot of Fig. 4. At lower temperatures, the behavior deviates from the usual Bloch T^5 behavior for electron–phonon interactions, instead exhibiting nearly T^2 behavior over the range 10–30 K. A fit over this range is shown in the inset plot of Fig. 4, for which the BG behavior obtained from the high-temperature fit described above was first subtracted, and the difference fitted to a T^2 temperature dependence. The T^2 coefficient resulting from this fit, $A=0.011\ \mu\Omega\ \text{cm/K}^2$, is displayed with the inset plot, and the drop in resistivity below T_c is also apparent in this plot. As alternative, an unrestricted fit of the raw data to $\rho(T)=\rho_0+AT^{\alpha}$ over this range yielded $\alpha=2.18$, showing that an exponent of nearly two best describes the data just above T_c.

T^2 resistivity behavior in ferromagnets may be due to magnon scattering or to spin fluctuations [12], however, its presence here above T_c signals the presence of spin fluctuations in this material. The magnitude of A is in the low end of the range for rare-earth intermetallics [13–15], indicating non-heavy Fermion behavior. In fact the magnitude is comparable to that of a number of d-electron intermetallics [16]. This points to the possibility that the T^2 behavior is due not to the development of valence fluctuations on the Ce ions but rather to correlations among d-based itinerant bands, which in turn may enhance the ferromagnetic coupling of Ce local moments that leads to the ferromagnetic ordering.

3.3. Thermal conductivity and thermopower

Fig. 5 shows the temperature dependence of the thermal conductivity for CeCuGe in the temperature range 10–300 K. As seen in the figure, $\kappa(T)$ increases with temperature and exhibits a maximum at about 30 K. The value of κ at $T=30$ K is about 130 mW/K cm which is of the same order as the corresponding maximum value (180 mW/K cm) observed for $CeAl_3$ [17], and is typical of polycrystalline materials. Thus, it appears that ordinary phonon behavior dominates throughout the range, with no anomalies near the magnetic transition.

The thermo-electric power (TEP) is a powerful technique which may reveal the electronic features of materials since it is a sensitive probe of energies near the Fermi surface. The temperature dependence of the TEP is plotted in Fig. 6. At low temperatures S is nearly linear in the temperature, as is typical for metals, while the decrease and eventual change in sign at higher temperatures may be attributed in part to phonon drag phenomena [18].

To better examine the low-temperature behavior of the TEP, the quantity S/T has been plotted in the inset of Fig. 6. For simple metals, the expected behavior is $S=\alpha T+\gamma T^3$, where the two terms are due to electronic and phonon drag mechanisms, respectively, [18]. Instead, we find that a much closer fit is obtained according to the function,

$$S = \alpha T + \beta T^2 \quad (1)$$

as is seen by the straight-line behavior of the inset plot. This behavior holds for the temperature range 10–30 K, over which the straight line was fitted. Below 10 K (the ferromagnetic T_c), a downturn in S can be seen, as is typical of magnetic metals [18].

Eq. (1) was, therefore, observed to apply over a temperature range of 10–30 K, and this is also the temperature range for which for which the resistivity followed a T^2 curve, as described above (Fig. 4). The TEP for intermediate-valent and Kondo materials depends on a number of parameters [19], however, Hirst [20] proposed a phenomenological model leading to the temperature dependence,

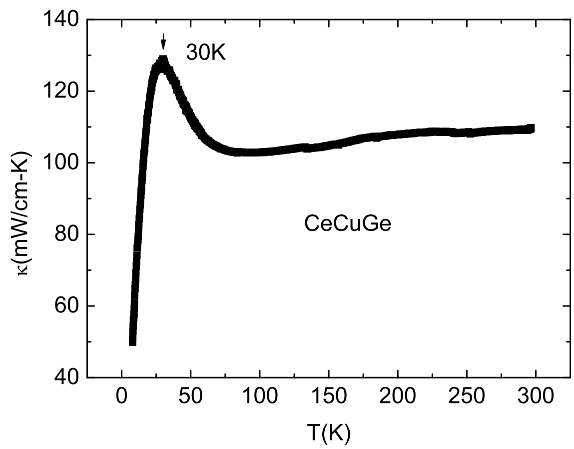

Fig. 5. Thermal conductivity (κ) versus temperature for CeCuGe.

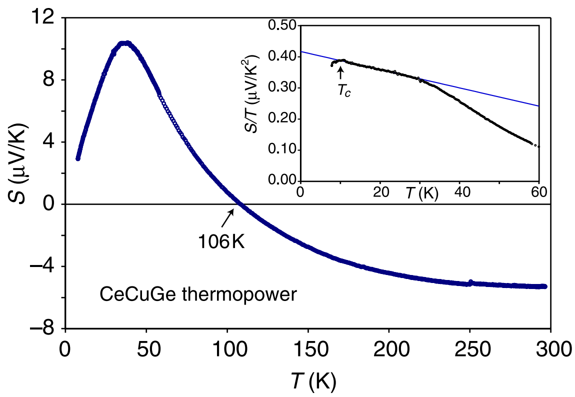

Fig. 6. The Seebeck coefficient (S) versus temperature for CeCuGe. Inset is a plot of S/T versus T, along with a best-fit straight line as described in the text.

$$S = \frac{\alpha T}{\beta^2 + T^2} \quad (2)$$

which provided a successful description of the TEP in some Ce-based materials [21,22]. Eq. (2) gives the behavior, $S/T = \alpha/(\beta^2 + T^2)$, which also trends downward with increasing T, but gives a fit to the data of Fig. 6 which is less faithful that provided by Eq. (1). Therefore, the source of the anomalous TEP behavior is not clear, however, since the temperature range matches that of the T^2 resistivity behavior, we tentatively associate this result with spin fluctuations above T_c.

4. Conclusions

Magnetization, magnetic susceptibility, electrical resistivity, thermal conductivity, and thermo-electric power measurements were carried out on CeCuGe. We observed a ferromagnetic transition with $T_c = 10$ K, identical to what was reported previously [3], however, the material exhibited soft ferromagnetic behavior below T_c, in contrast to the results of Ref. [3], which were interpreted to indicate the presence of strong magnetic anisotropy. Magnetization measurements indicate a fixed moment for Ce ions in this material above 53 K, below which temperature there is a reduction in the effective moment, attributed to a crystal-field-induced splitting. However, the resistivity exhibits T^2 behavior in the temperature range 10–30 K, above T_c, which we attribute to the development of spin fluctuations. In the same 10–30 K temperature range an anomalous behavior was observed in the thermo-electric power, which could be fitted to a $\alpha T + \beta T^2$ temperature dependence, and which is also presumably related to the development of spin fluctuations in the material.

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