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ORIGINAL PAPER

Magnetic Anomalies and Spin-Glass-Like Behavior in Ce_2CuGe_6

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Abstract A Ce-based intermetallic compound Ce_2CuGe_6 and its La analogue La_2CuGe_6 were synthesized and examined by X-ray powder diffraction, electrical resistivity, magnetic susceptibility, X-ray absorption spectrum and specific-heat measurements. The results reveal that Ce_2CuGe_6 is an antiferromagnetic Kondo-lattice compound with $T_N \sim 15$ K. The effective moment deduced from paramagnetic region is 2.58 μ_B per cerium ion, which is close to localized Ce^{3+} free ion in $^2F_{5/2}$ state. X-ray absorption measurement also precluded the existence of an intermediate valence state. The magnetic entropy calculated from heat capacity specific-heat measurement suggested a doublet ground state. In addition, we also observed a spin-glass-like behavior in this material. The spin-glass-like behavior might be due to the complex interplay between magnetic interactions.

Keywords Kondo lattice · Spin glass · X-ray absorption spectrum

1 Introduction

Studies of the competition between magnetic interaction and Kondo effect in rare-earth systems continue to be an active topic for decades. Among them, rare-earth element based ternary intermetallic compounds of the Re_2TX_6 type (Re = rare-earth element, T = transition metal, X = Si, Ge, and Sn) have been extensively studied, due to their remarkable physical properties. The crystallographic structure of Re_2TX_6 type compounds was first provided by Konyk et al. [1]. Subsequent researches have been focused upon this type of compounds for characterizing their properties [2–9]. Among these reports, Solobub et al. [2] made an extensive study about their crystal chemistry and magnetism. They found that all the compounds of this type exhibit antiferromagnetic phase transitions below 20 K and, in addition to the antiferromagnetism, the most distinct behavior is that some of them (Pr_2CuGe_6 and Nd_2CuGe_6) have a positive paramagnetic Curie temperature. They proposed that the positive paramagnetic Curie temperature might result from the formation of ferromagnetic layers, which are antiferromagnetically coupled. Tien et al. [4] studied the physical properties of Pr_2CuGe_6, in addition to the antiferromagnetism; they also observed a spin-glass-like behavior in this material. They suggested that such behavior might result from the competition of ferromagnetic and antiferromagnetic coupling between co-layers and adjacent layers.

These overall results characterize this type of compounds exhibiting interesting magnetic anomalies. Therefore, it is worth to further study their properties as well as the interplay among various interactions in the compounds. In this paper, a cerium-based Re_2TX_6-type compound Ce_2CuGe_6 was synthesized. Various measurements, including X-ray diffraction (XRD), temperature dependence of electrical resistivity, X-ray absorption spectroscopy (XAS), specific-heat, AC and DC susceptibility measurements were carried out in order to investigate its physical properties. Its isostructural compound La_2CuGe_6 was also synthesized and mea-

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sured in order to estimate the phonon contribution to the resistivity and specific heat.

2 Experimental Details

Polycrystalline bulk samples of Ce_2CuGe_6 and La_2CuGe_6 were synthesized by arc-melting from starting elements of at least 99.9% purity in their stoichiometric ratio under highly purified argon gas at one atmosphere pressure. These constituent elements were melted into a button. The arc-melted buttons were flipped over and re-melted several times to achieve homogeneity. The overall weight loss during melting was less then 0.5%. The buttons were then sealed in an evacuated quart tube and annealed at 800 °C for 3 days. The purities and structures of all samples were examined by powder X-ray diffraction (XRD) with a microcomputer-controlled X-ray diffractometer (Rigaku, D/MAX-2500) using monochromatic Cu Kα radiation ($\lambda \sim 1.542$ Å) at a step scan rate of 4 degrees per minute.

The electrical resistivity of the samples was measured by an LR-700 AC bridge using the four-probe method between 2 and 300 K in a cryostat fully automated for temperature and data acquisition. The DC magnetization studies were performed in a commercial SQUID magnetometer.[1] DC susceptibility was measured by both the zero-field-cooled (ZFC) and filed-cooled (FC) methods. For ZFC, the samples were cooled down from 300 to 1.8 K without applying any field and then applying a constant DC field at 1.8 K. Then, to measure the DC susceptibility in the constant field, the temperature was raised again. For FC, the samples were cooled down from 300 to 1.8 K in a constant DC field and then, to measure the susceptibility, the temperature was again raised. The temperature dependence of zero-field magnetization $M(T)$ was also performed in the SQUID magnetometer.

X-ray absorption near edge spectra (XANES) were carried out at the NSRRC (National Synchrotron Radiation Research Center, Hsinchu, Taiwan) on wiggler X-ray beamline BL17C by using a Si(111) double-crystal monochromator. The Ce L_{III}-edge XANES were obtained by the transmission mode in conventional ionization chambers. All samples were ground into fine powder to avoid thickness effect [10].

The AC susceptibility and specific heat were measured in a PPMS (physical property measurement system).[2] The temperature dependence of molar heat capacity ($C(T)$) was obtained by using the modified heat-pulse method in a temperature range between 1.8 and 40 K. The AC susceptibility measurements were performed in an AC 5-Oe driving field with the frequencies 100, 500, and 2000 Hz between 1.8 and 40 K.

[1]Quantum Design, Inc., San Diego, CA.

[2]See footnote 1.

3 Results and Discussion

Figure 1 displays the XRD patterns of Ce_2CuGe_6 and La_2CuGe_6. These patterns are consistent with the orthorhombic Ce_2CuGe_6-type structure, space group *Amm2*. The lattice parameters were determined by using the least-square-fitting method. The lattice parameters of Ce_2CuGe_6 are $a = 4.069(8)$ Å, $b = 4.216(3)$ Å, $c = 21.563(6)$ Å; and $a = 4.103(0)$ Å, $b = 4.265(6)$ Å, $c = 21.787(6)$ Å for La_2CuGe_6. These data are consistent with those reported previously [2, 7].

Figure 2 displays the temperature dependence of electrical resistivity of Ce_2CuGe_6 and La_2CuSi_6 between 1.8 and 300 K. The magnetic resistivity ρ_m, which is provided

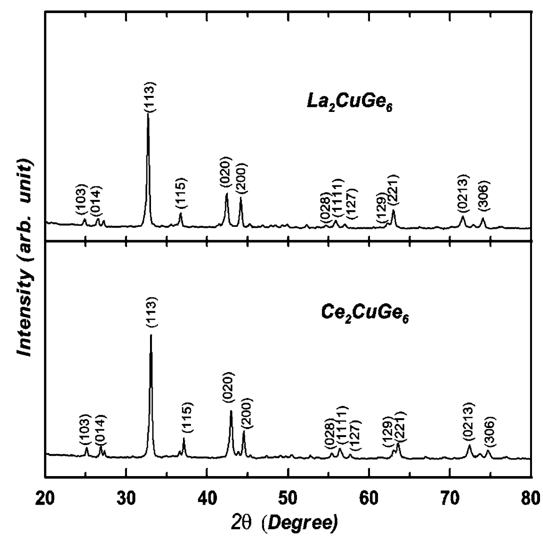

Fig. 1 X-ray diffraction patterns of Ce_2CuGe_6 and La_2CuGe_6

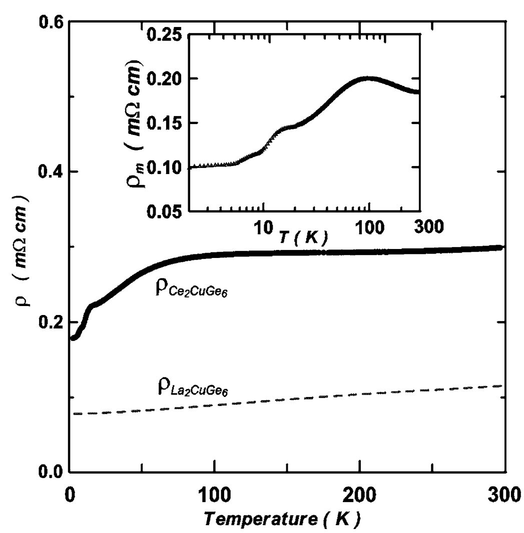

Fig. 2 Temperature dependence of electrical resistivity of Ce_2CuGe_6 and La_2CuGe_6 between 2 and 300 K. The *inset* is the magnetic resistivity ρ_m vs. $\log(T)$

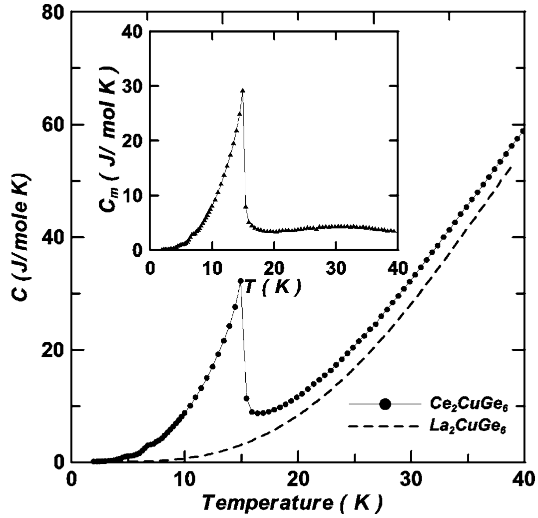

Fig. 3 Temperature dependence of specific heat $C(T)$ of Ce_2CuGe_6 and La_2CuGe_6 between 2 and 40 K. The *inset* plots the $C_m(T)$ between 2 and 40 K

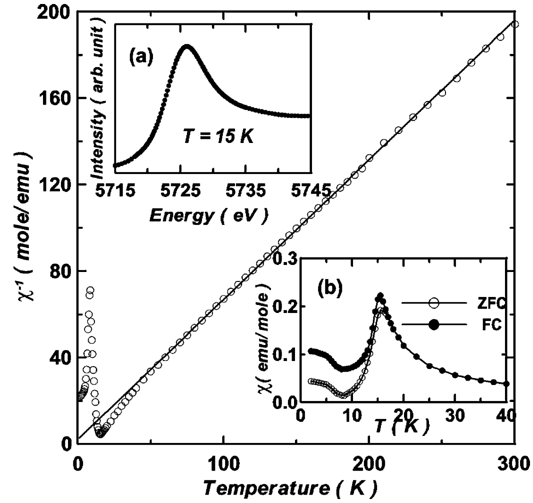

Fig. 4 Temperature dependence of the inverse of susceptibility χ_{ZFC}^{-1} of Ce_2CuGe_6 between 1.8 and 300 K at 200-Oe field. Inset **a** is the Ce-L_{III} edge XANES of Ce_2CuGe_6 at T = 15 K; inset **b** depicts $\chi_{ZFC}(T)(M)$ and $\chi_{FC}(T)(,)$ curves of Ce_2CuGe_6 between 1.8 and 40 K

in the inset, was obtained by subtracting the resistivity of the isostructural La_2CuGe_6. A $-\ln(T)$ dependence with a broad bump around 90 K can be observed, revealing the characteristic feature of a Kondo-lattice compound. It is generally agreed that this phenomenon is caused by scattering processes of the conducting electrons in the presence of crystal–field splitting, and the broad bump is associated with the Kondo effect on the entire multiplet. A steep decrease near 15 K can also be seen in the $\rho_m(T)$ curve. This anomaly is likely due to a magnetic ordering, which will be verified later by heat-capacity and magnetic-susceptibility measurements.

Figure 3 shows the specific heat versus temperature of Ce_2CuGe_6 and La_2CuGe_6 between 2 and 40 K. The magnetic contribution $C_m(T)$, which was obtained by subtracting the specific heat of La_2CuGe_6, is provided in the inset. A pronounced peak near 15 K can be observed. This prominent feature is believed to be resulting from an antiferromagnetic phase transition [2, 3, 7]. At low temperatures, a small bump near 6.5 K was observed. This anomaly can also be found in the resistivity measurement, which is probably due to an antiferromagnetic transition stemming from a small amount of Ce_2O_3, often reported in the literature on cerium compounds [11–13].

Figure 4 displays the temperature dependence of the inverse of susceptibility $\chi_{ZFC}^{-1}(T)$ between 1.8 and 300 K in 200-Oe field. The $\chi_{ZFC}^{-1}(T)$ follows the Curie–Weiss law above ~60 K with a negative Curie–Weiss temperature $\Theta_P \sim -3$ K. The effective moment deduced from the paramagnetic region is 2.58 μ_B per cerium atom, which is in agreement with the theoretical value of Ce^{3+} free ion in $^2F_{5/2}$ state. These results are close to the previous reports [2, 7].

Ce L_{III}-edge XANES is a very useful tool in deciding the valence of Ce for identifying an intermediate-valence system [10, 14]. Inset (a) of Fig. 4 depicts the Ce L_{III}-edge XANES at $T = 15$ K. The obtained Ce valence is 3.02, which corresponds to a 4f occupation $n_f \approx 0.98$, revealing a well localized character for the Ce 4f electron. Such a result can preclude the existence of an intermediate valence state, and it is also consistent with the result of obtained effective moment. Inset (b) shows the $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ curves of Ce_2CuGe_6 between 1.8 and 40 K in 200-Oe field. One can see that the DC susceptibility $\chi_{ZFC}(T)$ deviates from $\chi_{FC}(T)$ below $T \sim 17$ K, exhibiting a characteristic feature of a spin-glass system. In a spin glass, the spin-frozen temperature T_f can be identified as a temperature where $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ meet. However, irreversibility in DC susceptibility alone cannot conclude a spin-glass state; it could be a signature of some other complex magnetic structures. We still need further evidence to identify the spin-glass-like behavior.

Magnetic entropy calculation can provide another evidence for the spin-frozen phase. To estimate the magnetic entropy, we carried out the magnetic heat-capacity measurement. The C_m/T vs. T curves in 0, 10, and 30 kOe between 2 and 40 K are depicted in Fig. 5. The magnetic entropy S_m is the area below the curve, and it can be calculated by the relation

$$S_m = \int_0^{40\ \mathrm{K}} \frac{C_m}{T}\, dT.$$

All the estimated magnetic entropies for various fields are near a constant ~11.8 J mole^{-1} K^{-1}. This value is close to $2R\ln 2$, indicating a doublet ground state. The magnetic entropy calculated from $T = 0$ to $T_f \sim 17$ K in zero field

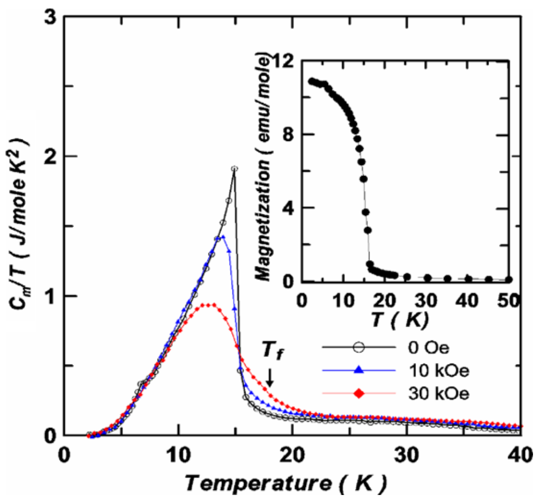

Fig. 5 The C_m/T vs. T of Ce_2CuGe_6 in 0, 10, and 30 kOe field between 2 and 40 K. The *inset* is the temperature dependence of magnetization $M(T)$ of Ce_2CuGe_6 between 2 and 50 K without any applied field

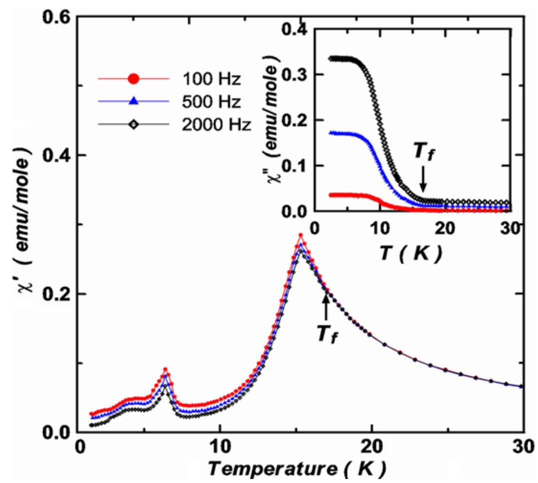

Fig. 6 Temperature dependence of real component of AC susceptibility χ' for Ce_2CuGe_6 in an AC field 5 Oe at 100, 500, and 2000 Hz between 1.8 and 30 K. The *inset* displays the imaginary component of AC susceptibility $\chi''(T)$

is about 9.4 J mole^{-1} K^{-1}, implying that about 79% of the degrees of freedom are lost or frozen out at T_f. For a simple antiferromagnetic material, the magnetic field will depress the magnetic order and shift the magnetic entropy toward a low-temperature region. However, as it is shown in Fig. 5, larger applied fields shift more magnetic entropy from low-temperature to high-temperature portion. Similar phenomenon was also reported in some canonical spin-glass systems [15–18]. The observation implies that the long-range antiferromagnetic order and the short-range spin-glass order might coexist in this system.

In a spin-frozen state, that a great fraction of magnetic entropy is forfeited above T_f is related to the ordering of ferromagnetic clusters which have already been formed above spin-frozen temperature. To verify the presence of the ferromagnetic clusters, we carried out the measurement of temperature dependence of magnetization ($M(T)$) without applying any field. As shown in the inset of Fig. 5, the magnetization starts to rise rapidly near 17 K, which might be due to the formation of the ferromagnetic clusters at that temperature.

Figure 6 displays the temperature dependence of χ' (real component of AC susceptibility) in an AC field of 5 Oe at 100, 500, and 2000 Hz, the imaginary part of AC susceptibility χ'' being provided in the inset. The $\chi'(T)$ curves exhibit pronounced maxima at $\sim$15 K, which correspond to the antiferromagnetic phase transition. Besides, a minor peak near 6.5 K can also be observed at 6.5 K, which corresponds to the antiferromagnetic phase transition of Ce_2O_3 impurity. The observations are also consistent with the specific-heat measurement. In addition, we noticed that the $\chi'(T)$ curves for different frequencies start to deviate below $\sim$17 K, and the $\chi''(T)$ curves start to increase steeply below $\sim$17 K. Such a frequency-dependent behavior in AC susceptibility was often reported for spin-glass systems [15–19]. However, judging from our AC susceptibility result, it is more likely that the antiferromagnetism and spin-frozen phase coexist in this material.

In the Ce_2CuGe_6-type structure the lattice constant c is much larger than a and b, hence its lattice can be considered as a layered structure. In such a lattice, the Ce^{3+} ions are located on layers separated by sheets of Cu and Ge. According to the proposal of Solobub et al. [2], the Ce^{3+} ions on the same layer might couple ferromagnetically to form the ferromagnetic clusters, and the ferromagnetic clusters which are in adjacent layers are likely to correlate antiferromagnetically. The competition between these two forms of coupling will probably give rise to the spin-glass-like behavior. In addition, because our samples are polycrystalline, it will further enhance the disorder of the magnetic coupling. The interplay of these interactions might lead to spin-order frustration in the system. Spin-order frustration, which is the basic ingredient of a spin-frozen state, is indispensable in order to establish the competing and to ensure the cooperativeness of the freezing process. This mechanism can also account for the ferromagnetic behavior in the temperature dependence of magnetization $M(T)$. Furthermore, the fact that the paramagnetic Curie temperature Θ_P is close to zero can also account for the fact that the competitions between ferromagnetic and antiferromagnetic interactions are compatible in the system.

4 Conclusion

A Ce-based intermetallic compound Ce_2CuGe_6 and its isostructural compound La_2CuGe_6 were synthesized and examined by XRD, XANES, electrical resistivity, DC and AC magnetic susceptibility, as well as heat capacity measurements. The results reveal that Ce_2CuGe_6 is an antiferromagnetic Kondo lattice as reported before. In addition, we also observed a spin-glass-like behavior from our DC magnetic susceptibility measurement. This behavior was further confirmed by heat-capacity and AC magnetic-susceptibility measurements. The spin-frozen state might result from spin order frustration, attributed to the complex interplay of magnetic interactions. Our present work also suggests that Ce_2CuGe_6 is a spin glass. However, further experiments, for example neutron scattering, might be needed to clarify this possibility.

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