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Magnetism and electronic transport properties of Ce_5CuPb_3

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Polycrystalline sample of the ternary Ce-based compound Ce_5CuPb_3 was prepared and characterized using room temperature powder X-ray, EDX analysis as well as by magnetic susceptibility, electrical resistivity, and thermoelectric power measurements. The compound crystallizes in the Ti_5Ga_4-type structure (space group $P6_3/mcm$) with two different cerium sites: one at the 4d and the other at 6g position. The susceptibility shows two successive magnetic phase transitions at $T_{C1} = 46.0 \pm 0.5$ K and $T_{C2} = 5.0 \pm 0.5$ K. The double magnetic phase transition may be explained by two inequivalent magnetic sublattices of Ce^{3+} ions. The analysis of the magnetic data suggests that the transition at T_{C1} is of ferromagnetic origin and at T_{C2} is of ferrimagnetic one. Both the magnetic susceptibility, and electrical resistivity data imply the localized character of the Ce 4f electron. Above 150 K the $\chi(T)$ data follow the Curie–Weiss law with the effective moment $\mu_{\text{eff}} = 2.69$ μ_B/Ce and the paramagnetic Curie temperature θ_p equal to –21.8 K. The electrical resistivity exhibits a clear anomaly at T_{C1}, below which the resistivity sharply decreases due to the reduction in the spin–disorder scattering. The thermoelectric power (TEP, S) of Ce_5CuPb_3 is negative over the temperature range studied, reaching the value of –14 μV/K at room temperature, and weakly varying with decreasing temperature down to T_{C1}. A rapid change in TEP occurs below 25 K with the slope S/T as large as –0.27 μV/K^2.

Key words: successive magnetic phase transitions; magnetic properties; electron transport properties; Ce_5CuPb_3

1. Introduction

Ternary rare earth (R) plumbites R_5CuPb_3 were reported to crystallize in a hexagonal Ti_5Ga_4-type structure (space group $P6_3/mcm$) [1]. These intermetallics, with the chemical 5:1:3 stoichiometry, are characterized by two different sites for the R ions located at 4d and 6g, respectively. Amongst these compounds, only Dy_5CuPb_3 has been studied so far with respect to its magnetic and electron transport properties [2]. It has been argued that in this alloy there are complex magnetic phase transitions, ferromagnetic below 45 K and ferrimagnetic below 6.5 K. The magnetism is believed

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to result from the localized Dy^{3+} ions. In this contribution, we report on the results of experimental investigation of an other member of the R_5CuPb_3 family, namely Ce_5CuPb_3. From magnetic and electron transport measurements, we show that the behaviour of Ce_5CuPb_3 is similar to that of Dy_5CuPb_3, e.g., Ce ions behave as localized ones. Therefore, the character of the Ce 4f electrons in Ce_5CuPb_3 seems to be different from that in other previously studied 513 Ce-based compounds, Ce_5CuSn_3 [3], Ce_5CuSb_3 [4] and Ce_5CuBi_3 [5]. These latter compounds exhibit heavy fermion behaviour, reflected by a large Sommerfeld ratio C_p/T at low temperatures. We also argue that the magnetic properties of the Ce_5CuM_3 (M = Sn, Bi and Pb) series of compounds depend both on the Ce–Ce exchange interaction and strength of the hybridization between the 4f and conduction electrons.

2. Experimental details

Several specimens of Ce_5CuPb_3 were prepared by arc-melting of stoichiometric amounts of high-purity elements (Ce 99.9 wt. %, Cu 99.999 wt. % and Pb 99.999 wt. %) in a Ti-gettered pure argon atmosphere. The specimens were remelted several times to ensure homogeneity. After annealing at 800 °C for one week, the specimens were examined by X-ray powder diffraction at room temperature. The observed Bragg peaks can be indexed to the hexagonal structure with the space group $P6_3/mcm$. The refined lattice parameters are: a = 9.551(2) Å and c = 6.776(2) Å being comparable to those previously reported [1]. The composition of the obtained samples was established using an energy dispersive X-ray analysis. It turns out that in addition to the major 513 phase, there exists a small quantity of free Pb. The data reported in this work were done on the sample containing the Pb contamination lower than 2%.

Dc magnetization measurements were carried out with a Quantum Design SQUID magnetometer in fields up to 5.5 T and in the temperature range 2–400 K. The electrical resistivity was measured by the standard dc four-probe technique in the temperature range 2–300 K. The sample was rectangular with typical dimensions $0.5\times0.5\times5$ mm^3. The voltage and current leads were attached with a silver paste. Thermoelectric power was measured using a differential method in the temperature range 4–220 K. The temperature gradient of about 2 K was applied across the sample length, using an Au–Fe (7%) chromel thermocouple. The relative resolution of the experimental setup reached 10 nV and the absolute accuracy of the presented data was as low as 5% over the studied temperature range.

3. Experimental results and discussion

The temperature dependence of the magnetic susceptibility of Ce_5CuPb_3 measured at the field of 0.5 T and in the temperature range 150–400 K (not shown here) can be described by the Curie-Weiss law:

$$\chi(T) = \chi(T) = \frac{N\mu_{\mathrm{eff}}^{2}}{3k_B\left(T-\Theta_p\right)}$$

with an effective moment μ_{eff} = 2.69 μ_B/Ce and a paramagnetic Curie temperature θ_p equal to –21.8 K. The experimental value of μ_{eff} is close to the Russell–Saunders value for a free Ce^{3+} ion (2.54 μ_B), designating the localized character of the Ce 4f-electron. A negative value of θ_p may indicate the existence of antiferromagnetic exchange interaction in the studied compound. At low temperatures, the $\chi(T)$ curve shows a step-like increase (Fig. 1a), giving clear evidence of the occurrence of magnetic phase transitions. In Figure 1 b, we display the temperature derivative of the susceptibility, where we observe two anomalies at T_{C1} = 46.0 ± 0.5 K and T_{C2} = 5.0 ± 0.5 K (indicated by arrows). Tentatively, we attribute these anomalies to ferromagnetic-like transitions. In the same manner as in the case of Dy$_5$CuPb$_3$ [2], the double magnetic phase transition may be explained by existence of two inequivalent magnetic sublattices of the magnetic ions.

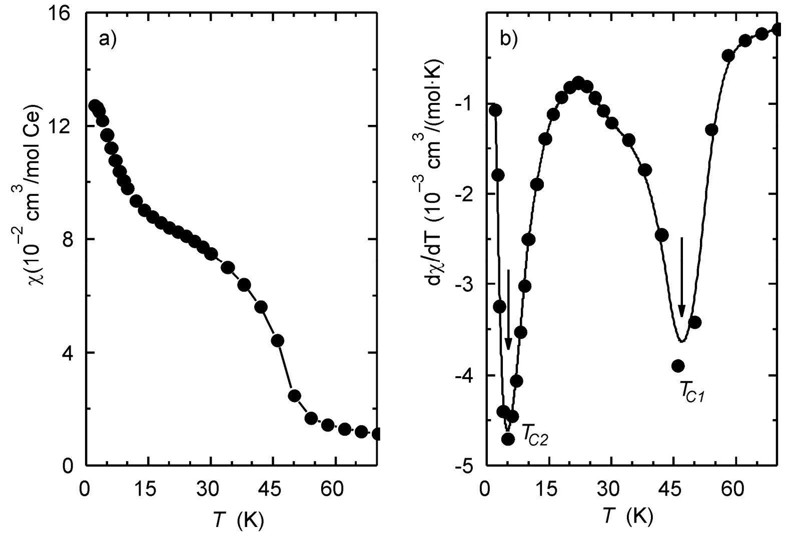

Fig. 1. Temperature dependence of the magnetic susceptibility of Ce$_5$CuPb$_3$ (a), and the derivative $d\chi/dT$ as a function of temperature (b). The arrows indicate the magnetic phase transitions

In the upper panel of Fig. 2 we show the magnetization data collected at temperatures 2 K and 5 K, i.e., below T_{C2}. For a clarity of the presentation, the data are vertically shifted. One can see that the initial magnetization is linear and is fitted with the solid line. The linear dependence M vs. H is observed up to 0.5 T for T = 2 K and 0.15 T or T = 5 K. Moreover, these low-temperature data distinguish themselves by a hysteresis, which appears below 1 T. These features imply a ferri- or antiferromagnetic character of the transition at T_{C2}.

The lower panel of Fig. 2 presents magnetization data taken between 10 K and 75 K. As can be seen, the data collected between T_{C2} and T_{C1} (at 10, 25 and 40 K) show spontaneous magnetization. Such a behaviour is consistent with the magnetic phase transition of the ferromagnetic origin at T_{C1}. However, it is noted that the magnetization does not saturate even at the highest applied magnetic field strength of 5 T. This observation hints that only a part of the Ce ions undergo a transition into the ferromagnetic state.

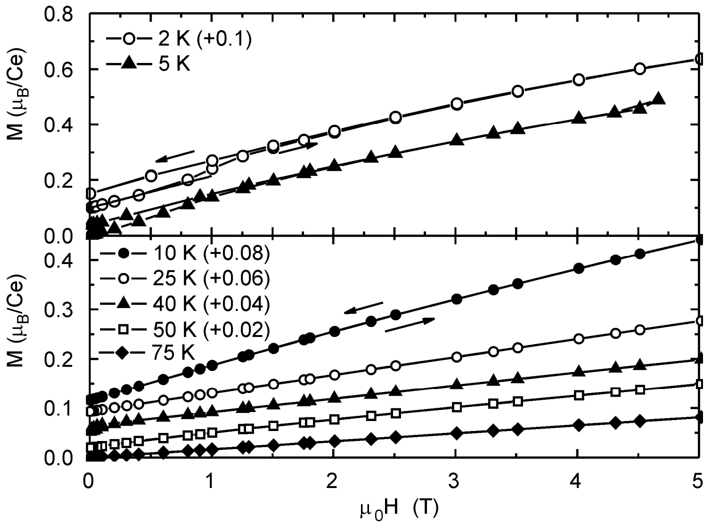

Fig. 2. Magnetization of Ce_5CuPb_3 measured below 75 K. For clarity of presentation, the data collected at 2, 10, 25, 40 and 50 K are shifted upwards by values given in the figure. The arrows indicate increasing or decreasing magnetic field strength

The temperature dependence of the electrical resistivity of Ce_5CuPb_3 shown in Fig. 3a displays a sharp decrease around T_{C1}. Such a decrease is usually attributed to the reduction of spin-disorder scattering. However, it is hard to detect the anomaly associated with the transition at T_{C2}, since the resistivity measurements performed on several synthesized samples of Ce_5CuPb_3 have shown systematic presence of a severe drop in the resistivity at 6.5 K, due to the superconductivity of free lead in the samples. Further investigations, notably the measurements of the specific heat and Hall effect, should provide additional information on the anomalous resistivity behaviour of Ce_5CuPb_3. It should be added that the superconductivity appearing in our samples can be eliminated by measurements in a magnetic field of about 0.05 T. Because of micro-cracks and the oxidation problem, the geometric dimension cannot be exactly determined, thus the absolute values of the measured resistivity should be taken with great caution.

The thermoelectric power of Ce_5CuPb_3 (Fig. 3 b) is negative in the whole temperature range under investigation. As can be seen, the thermopower displays a minimum around T_{C1} followed by a linear temperature dependence, representing the diffusion thermopower. It is interesting to note that the slope *S*/*T* in the temperature range 6–22 K reaches the value as large as –0.27 μV/K^2. From the close relationship between the ratio *S*/*T* and C_p/T observed for a number of intermetallics [10], one may expect an enhancement in the electronic specific heat of Ce_5CuPb_3. However, an alternative interpretation may be provided, related to a change in the electronic structure due to a magnetic phase transition below T_{C1}.

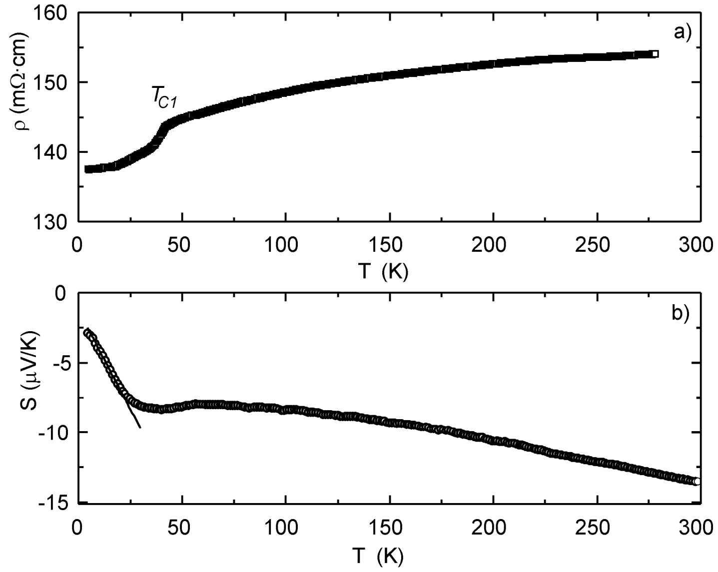

Fig. 3. Temperature dependence of the electrical resistivity (a), and thermoelectric power (b) of Ce_5CuPb_3 as a function of temperature. The solid line (below 25 K) illustrates a high slope *S*/*T*

4. Concluding remarks

We measured magnetization, electrical resistivity and thermoelectric power of polycrystalline samples of the Ce-based intermetallic compound Ce_5CuPb_3. The experimental data indicate two successive magnetic phase transitions at $T_{C1} = 46.0 \pm 0.5$ K and $T_{C2} = 5.0 \pm 0.5$ K, caused by Ce–Ce exchange interactions in two different Ce sites. Combined with the previously reported data [3–5], the present results point to a clear influence of the ligands on the magnetic properties of investigated compounds. The fact that the compounds with M = Sn and Bi are found to order at lower temperatures and with a lower effective moment compared to those of Ce_5CuPb_3, may indicate a more localized character of the Ce 4f electrons in the latter compound. This behaviour can be anticipated from the change in the unit cell volume, systematically increasing across the series with M = Sn, Bi and Pb. The increase of the distance between the magnetic central and nonmagnetic ligand ions certainly weakens the hybridization between 4f and conduction electrons, and in consequence strengthens the localized electron magnetism.

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