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A unique metallic system $Ce_3Pt_{23}Ge_{11}$

R. Troć[a,*], D. Kaczorowski[a], T. Cichorek[a], B. Andraka[b], R. Pietri[b],
Yu. D. Seropegin[c], A.V. Gribanov[c]

[a] *W. Trezebiatowksi Institute for Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 937, 50-950 Wroclaw 2, Poland*

[b] *Department of Physics, University of Florida, Gainesville, Florida 32611, USA*

[c] *Chemistry Department, Moscow State University, 119899 Moscow, Russian Federation*

Abstract

A novel ternary compound $Ce_3Pt_{23}Ge_{11}$ crystallises in a new structure type with space group $F\bar{4}3m$ and $a = 1.71833(9)$ nm. Here we present the results of magnetic, electrical and specific heat measurements, obtained on the single crystal and polycrystalline samples. This compound is a metal with normal Ce^{3+} magnetic behaviour. Although the specific heat at low temperatures rises rapidly to a large value of 2.5 J/Ce-mol K at 0.38 K, we have not detected any phase transition down to this temperature. Only in the temperature range 0.1–1 K a small decrease in the resistivity value can be detected with an inflection point at approximately 0.3 K.

Keywords: Cerium intermetallics; Magnetic susceptibility; Electrical resistivity; Heat capacity

1. Introduction

Intermetallic compounds from the ternary systems Ce–T–M (T is a transition metal and M = Si or Ge) are known to exhibit a number of interesting properties such as heavy-fermion superconductivity, Kondo-lattice behaviour, anomalous magnetism or intermediate valency. In a previous paper [1] a new ternary compound $Ce_3Pt_{23}Ge_{11}$ was found to exist. X-ray single crystal studies showed this compound to crystallise in cubic structure with the lattice parameter $a = 1.71833(9)$ nm, $Z = 8$ and space group $F\bar{4}3m$. The coordination polyhedron of the cerium atoms is a compressed cube (parallelepiped) with two square facets. It has eight Pt-apexes, with two slightly different Ce–Pt distances, namely 0.3182 and 0.3206 nm. We report herein the results of magnetic, transport and specific heat measurements performed on this compound in single-crystal and polycrystalline forms.

2. Experimental details

A polycrystalline sample of $Ce_3Pt_{23}Ge_{11}$ was prepared from the starting mixture of composition in atomic percent: 8Ce, 62Pt and 30Ge. Purity of the elements was Ce, 98 wt.%; Pt, 99.9 wt.%; and Ge, 99.999 wt.%. The mixture was arc-melted in an argon atmosphere and then annealed at 600°C for 600 h. X-ray powder diffraction showed only the presence of a single phase. The lattice constant was close to the value found in single crystal measurements [1].

Crystal growth was conducted in a vertical-tube electrical furnace. The sample was moved with a velocity of 0.3 mm h^{-1} in the temperature gradient of the growth zone of 150°C cm^{-1} with an maximum temperature applied of 1070°C. The mass of the sample was 10 g. After the process, single crystals having

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[*] Corresponding author.

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maximum dimensions of approx. 3 × 3 × 3 mm^3 were separated mechanically under a microscope.

The magnetic susceptibility was measured using a SQUID magnetometer at temperatures of 1.7–300 K, while the magnetisation was taken at temperatures 1.7, 2.5 and 5 K and in magnetic fields up to 5 T. The electrical resistivity was measured down to 20 mK by a conventional DC four-probe technique. Only polycrystalline sample was measured. The dimension of the sample used was 0.5 × 0.3 × 3 mm^3. The accuracy of electrical resistivity measurements in the temperature region 4.2–300 K was 1 μV, while that between 20 mK and 4.2 K was 10 nV. The specific heat was measured by a relaxation method between 0.38 and 10 K. The data below 1 K were taken with a calorimeter placed in a ^{3}He refrigerator. The results obtained for the polycrystalline and single crystalline samples were close to each other within the experimental error.

3. Results

The susceptibility (χ) measurement results obtained on a single crystal of $Ce_3Pt_{23}Ge_{11}$ are shown in Fig. 1. They were similar to those found on the polycrystalline sample. χ follows a Curie–Weiss law at higher temperatures, i.e. above approx. 150 K. A relatively strong crystal field effect is seen below this temperature. The high temperature effective magnetic moment μ_{eff} and the paramagnetic Curie temperature Θ_p are 2.51 μ_B and 0.5 K, respectively. The derived moment is nearly equal to that of free Ce^{3+} ion.

The magnetisation measurement results are given in Fig. 2. As this figure illustrates, an increasing curvilinear character of the magnetisation with decreasing temperature is observed. However, no hysteresis and remanence have been detected in these

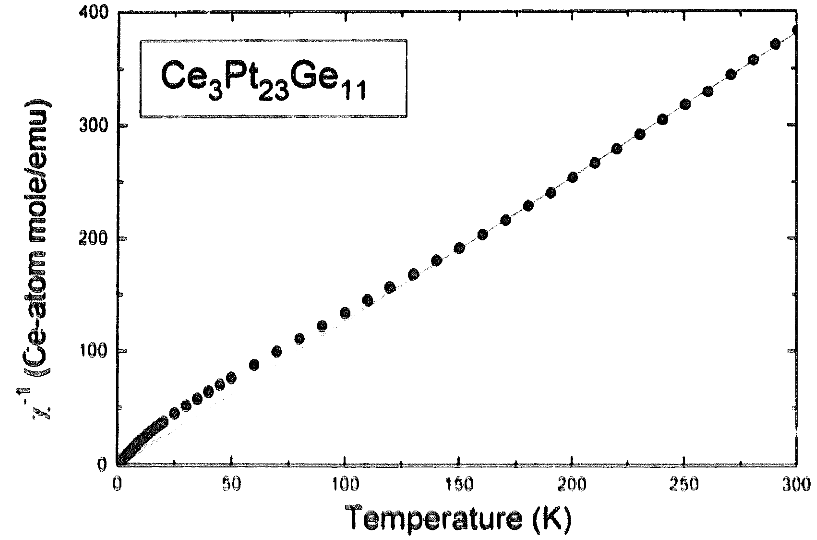

Fig. 1. Temperature dependence of the reverse magnetic susceptibility of $Ce_3Pt_{23}Ge_{11}$.

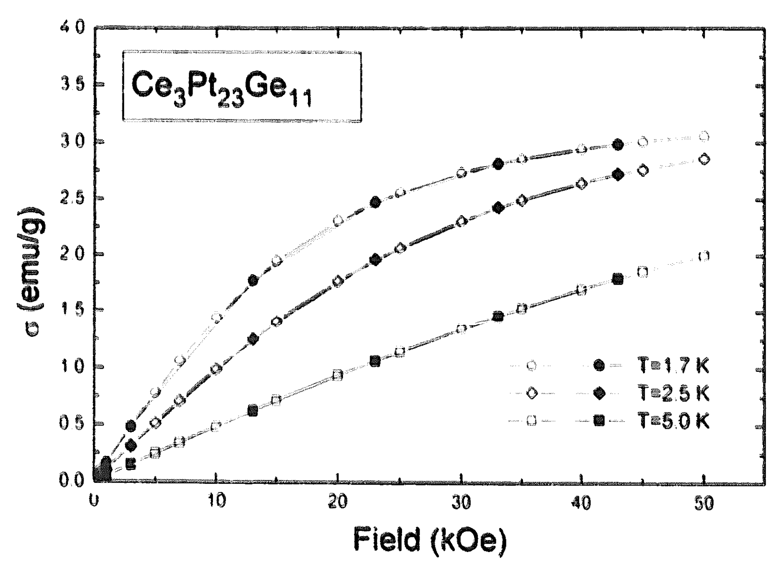

Fig. 2. Magnetisation up to 5 T for $Ce_3Pt_{23}Ge_{11}$ at three temperatures: 1.7, 2.5 and 5.0 K.

measurements. The magnetisation curve at 1.7 K shows almost saturation in an applied field of 5 T. Calculated magnetic moment at this field is 1.05 μ_B. This means that an applied field reaches the saturation moment in the paramagnetic state relatively easily. Thus, the magnetisation curves in the non-ordered state are qualitatively as expected for the Γ_6 doublet as a ground state and the Γ_8 quartet as an excited state. Although the magnetisation of the Γ_7 doublet, described by the equation:

$$\mu_{\Gamma_7} = gJ\mu_B tgh\left(\frac{gJ\mu_B}{kT}\right),$$

with $J = 1/2$ and spectroscopic splitting factor $g = 10/7$, gives only $\mu_s = 0.714$ μ_B/Ce-atom, the moment close to 1.0 μ_B at B = 5 T is calculated assuming a crystal field splitting value, Δ_{CF}, between Γ_7 and Γ_8 of several tens K. For a value $\Delta_{CF} \approx 60$ K we find an approximate agreement with the low-temperature χ^{-1} vs. T experimental curve.

The temperature variation of the electrical resistivity of $Ce_3Pt_{23}Ge_{11}$ is shown in Figs. 3 and 4. The overall character of this variation is typical of metallic system. At low temperatures the resistivity goes to the constant low value, but below 0.4 K (see the inset Fig. 4) the resistivity decreases slightly and again reaches a constant value at still lower temperatures. As will be shown below, this small jump in the resistivity may reflect a transition to the magnetically ordered state. However, at this point we cannot classify what kind of a phase transition occurs.

Fig. 5 shows the specific heat data, which above 4.2 K are typical of those for non-magnetic metallic systems. The least squares fit performed between 4.2 and 8 K on the data in the form of C/T vs. T^2 yields the following values for the electronic specific heat coefficient and Debye temperature, 10 ± 2 mJ/Ce-mol K^2 and 230 K, respectively. The value of the electronic coefficient is in the range of values found in many metallic compounds and alloys. However, this assertion is incompatible with the specific heat at lower temperatures and also with the magnetic susceptibility. The temperature dependence of the specific heat below 3 K changes drastically; the specific heat increases with a decrease of temperature hinting at some phase transition occurring at very low temperatures. However, we have not detected any phase transition down to the lowest temperature of our study, 0.38 K. At this temperature, C/T reaches a huge value of approx. 6.6 J/Ce-mol K^2. The total entropy removed between 0.38 and 10 K is less than 0.25 Rln2 per mole of Ce. Thus $Ce_3Pt_{23}Ge_{11}$ is a unique metal-

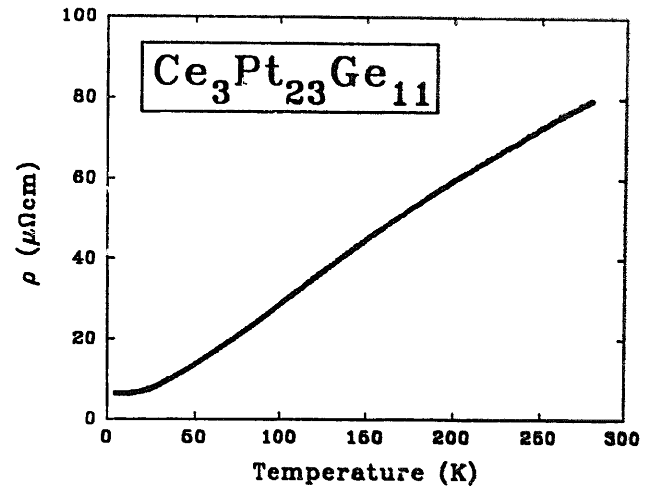

Fig. 3. Temperature dependence of the electrical resistivity of $Ce_3Pt_{23}Ge_{11}$ in the temperature range 4.2–300 K.

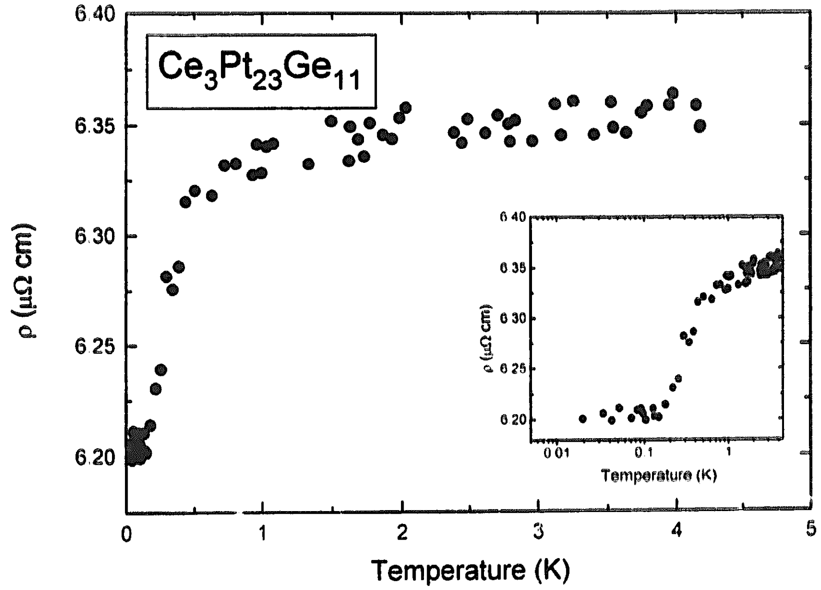

Fig. 4. Low temperature electrical resistivity of $Ce_3Pt_{23}Ge_{11}$ down to 20 mK. The inset shows ρ as a function of log T.

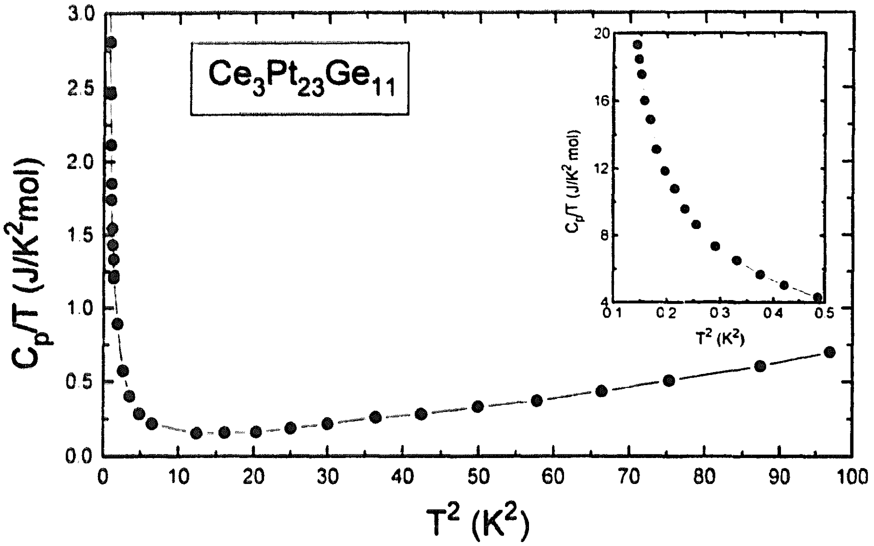

Fig. 5. Specific heat per cerium mole of $Ce_3Pt_{23}Ge_{11}$ plotted in the form C_p/T vs. T^2. The inset shows the same function at low temperatures.

lic system, in which almost free Ce^{3+} moments persist to very low temperatures. Measurements at still lower temperatures are needed to determine the nature of the ground state.

4. Discussion

$Ce_3Pt_{23}Ge_{11}$ belongs to a small group of Ce-compounds having puzzling magnetic properties at the lowest temperatures. Only two Ce-compounds, namely heavy fermion compound: $CeCu_6$ [2] and $CePt_2Si_2$ [3] are known to exhibit no static ordering (magnetic or superconducting) at the lowest temperatures.

$Ce\ Pt_{23}Ge_{11}$ resembles two other cubic Ce-compounds also containing a large number of atoms, namely $Ce_3Pd_{20}Si_6$ [4,5] and $Ce_3Pd_{20}Ge_6$ [6,7]. The magnetic part of the specific heat divided by temperature of $Ce_3Pd_{20}Si_6$, C_m/T, forms a peak as high as 9 J/Ce-mol K^2 at 0.2 K. This peak, based on AC-susceptibility, has been assigned to a spin-glass freezing at 0.15 K. It was also found that the magnetic field strongly depresses C_m/T at low temperatures. On the other hand, the isostructural Ge-counterpart to the above silicide, $Ce_3Pd_{20}Ge_6$, also demonstrates a sharp peak in the specific heat at somewhat higher temperature 0.7 K, but this time due to an antiferromagnetic ordering. The type of ordering in this latter compound has been confirmed by AC-susceptibility and electrical resistivity measurements [6]. Moreover, another transition observed at 1.2 K has been described as due to a quadrupolar ordering. This in turn suggests that the Γ_8 quadruplet is the crystal-field ground state in $Ce_3Pd_{20}Ge_6$ [7].

In conclusion, $Ce_3Pt_{23}Ge_{11}$ is a metallic compound having trivalent Ce ions. The observed huge value of the specific heat at $T = 0.38$ K suggests the possibility of a magnetic transformation to some ordered or spin-glass state just below this temperature. A unique aspect of this compound is that the eventual competition between magnetic interaction and Kondo effect is here on a very small energy scale, which marks out this compound from other ternary Ce-intermetallics.

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