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Heavy fermion like behavior in layered Ce-based oxysulfides

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Abstract

We have succeeded to obtain an almost single phase of layered oxysulfide CeOCuS and found a heavy fermion like behavior in this compound. It crystallizes in tetragonal LaOAgS-type structure and the lattice parameters a and c are 0.3923 and 0.8333 nm, respectively. They are smaller than those expected for trivalent Ce ion. This suggests that Ce ions exist in a mixed valence state. The temperature dependence of the specific heat, C shows an upturn below about 7 K. It is expressed by the following relation, $C = \gamma T + \beta T^3 + \delta T^3 \ln T$. The value of γ is about 324 mJ/mol K^2, which is comparable with that of conventional heavy fermion compounds. The temperature dependence of the electrical resistivity is metallic and obeys the following relation, $\rho = \rho_0 + \rho_1 T^2 + \rho_2 T^2 \ln T$, below 100 K. The temperature dependence of the magnetic susceptibility is expressed by the sum of Pauli paramagnetic and Curie Weiss terms. The Pauli paramagnetic term has a large value, which corresponds to about 10% that estimated from γ. The effective magnetic moment μ_{eff}, 1.62μ_{B}, is smaller than the free ion value of trivalent Ce and indicates about 64% of Ce ions is trivalent.

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Keywords: Layered oxysulfides; Heavy fermion; Magnetic properties; Specific heat; Electrical resistivity

1. Introduction

Layered oxysulfide ROCuS where R is a rare earth element has a LaOAgS-type crystal structure, in which RO and CuS sheets are stacked along c-axis alternately (tetragonal system; space group $P4/nmm$) [1]. In $La_{1-x}Ca_xOCu_{1-x}Ni_xS$ where a part of La and Cu sites is substituted by Ca and Ni simultaneously in LaOCuS, we have previously observed a metal–semiconductor transition for the first time [2]. We have also observed a weak ferromagnetism with a Curie temperature exceeding room temperature in the above system [3]. Though the crystallographic study of many ROCuX (X: S, Se, Te) compounds was recently carried out [4], their physical properties were not reported. We investigated the electrical and magnetic properties of ROCuS (R: Pr, Nd) and showed that both compounds are semiconductive and their magnetic properties are well explained by trivalent rare earth ion [5].

As for CeOCuS, Charkin et al. [4] reported that a considerable nonstoichiometry for Cu ions was found and concluded that it was due to the mixed valence of Ce ions. However, we have succeeded to prepare an almost single phase of a little Ce deficient CeOCuS. In this study, we report the preparation method and electrical, magnetic and thermal properties of this compound.

2. Experimental

Samples were prepared by the solid state reaction. The raw materials were CeO_2, Ce_2S_3, CuO and Cu powders. Two kinds of the samples were prepared. One was a stoichiometric sample and the other was 5% CeO_2 deficient one. These powders were thoroughly mixed in Ar atmosphere and pressed into bars. They were first heated at 900 °C in an evacuated quartz tube (about 10^{-3} Pa) for 40 h and heated again with an excess amount (2%) of sulfur under the same condition.

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X-ray powder diffraction was measured by Rigaku RINT1100 system and the data were analysed by Rietveld method with Rietan 2000 program [6].

The magnetization, the electrical resistivity and specific heat are measured with Quantum Design PPMS 7N system.

3. Results and discussion

Fig. 1 shows the powder X-ray patterns of two samples mentioned above. While rather strong peaks due to the impurity phase CeO_2 are observed in the stoichiometric sample, the 5% CeO_2 deficient sample is considered to be almost single phase although a trace of CuS is observed. The lattice parameters of the latter, a and c, are 0.3923 and 0.8333 nm, respectively. They are smaller than those expected from the curve of the lattice parameters vs. atomic number of other ROCuS with trivalent R ions [4,5]. This suggests that Ce ions exist in a mixed valence state.

Fig. 2 shows the temperature dependence of the specific heat C between the temperature range $3 < T < 300$ K, and inset shows that below 10 K. The value of the specific heat at 300 K of 94.6 J/mol K is about 95% of $12R$, where R is a gas constant. The temperature dependence shows a minimum at about 7 K and an upturn below this temperature. Such upturn is not observed in other ROCuS of which magnetic properties are explained by trivalent rare earth ions [5]. The C/T versus T^2 curve below 20 K is shown in Fig. 3. The extrapolated value to $T^2 = 0$ which gives an electron specific heat coefficient γ is about 324 mJ/mol K^2. This is comparable with that of conventional heavy fermion compounds. Then, the upturn of the specific heat is analyzed by the following equation:

$$C = \gamma T + \beta T^3 + \delta T^3 \ln T. \qquad (1)$$

The obtained linear relation shown in Fig. 4 suggests that this system is a three dimensional fermi liquid [7].

Fig. 5 shows the temperature dependence of the electrical resistivity between the temperature range $3 < T < 300$ K and inset shows that below 100 K. While other ROCuS is

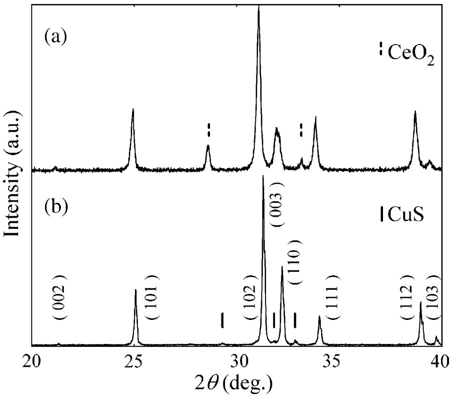

Fig. 1. The powder X-ray diffraction pattern of (CeO)CuS: (a) stoichiometric sample and (b) 5% CeO_2 deficient sample.

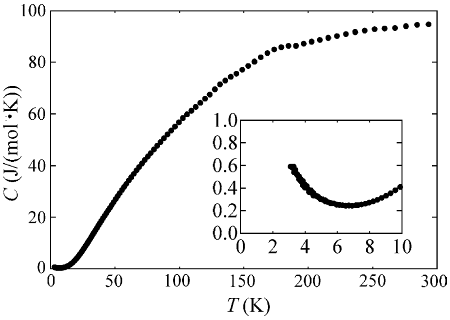

Fig. 2. The temperature dependence of the specific heat between the temperature range $3 < T < 300$ K. Inset shows the low temperature part below 10 K.

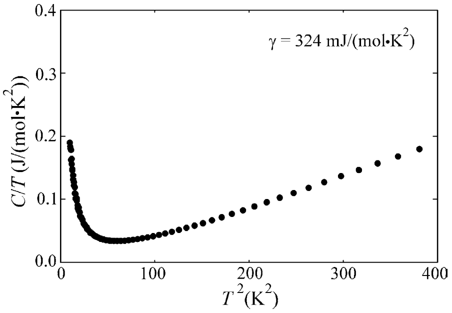

Fig. 3. The C/T vs. T^2 curve below 20 K.

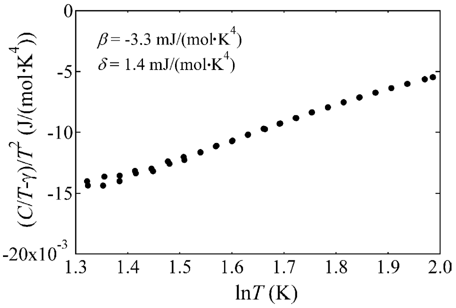

Fig. 4. The $(C/T - \gamma)/T^2$ vs. $\ln T$ curve below about 7 K.

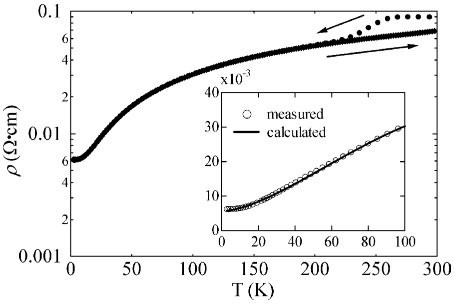

Fig. 5. The temperature dependence of the electrical resistivity between the temperature range $3 < T < 300$ K. Inset shows a low temperature part below 100 K and the solid line is theoretical value calculated from Eq. (2).

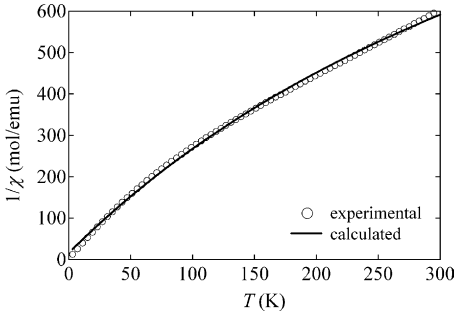

Fig. 6. The temperature dependence of the inverse magnetic susceptibility between the temperature range $3 < T < 300$ K. The solid line is theoretical value calculated from Eq. (3).

semiconductive [5], CeOCuS is metallic and the temperature dependence below 100 K is well fitted by the relation:

$$\rho = \rho_0 + \rho_1 T^2 + \rho_2 T^2 \ln T \tag{2}$$

with $\rho_0 = 5.94 \times 10^{-3}$, $\rho_1 = 1.43 \times 10^{-5}$ and $\rho_2 = -2.59 \times 10^{-6}$. First term corresponds to the residual resistance, and second and third terms to electron–electron scattering. This temperature dependence also suggests that the present system is a three dimensional fermi liquid. While a hysteresis is observed above about 230 K, its origin is not elucidated now.

Fig. 6 shows the temperature dependence of the inverse magnetic susceptibility between the temperature range $3 < T < 300$ K. It is rather concave. As the crystal field effect (CEF) becomes dominant at low temperature for other ROCuS, the origin of the observed curved behavior over a wide temperature range is not considered to be CEF.

Then, firstly, the magnetic susceptibility is analyzed by the sum of temperature independent Pauli paramagnetic term and Curie Weiss term:

$$\chi = \chi_P + \frac{C}{T - \theta_P}. \tag{3}$$

where χ_P, C and θ_P is Pauli paramagnetic susceptibility, Curie constant and paramagnetic Curie temperature, respectively. The values of χ_P, C and θ_P obtained from the best fit are 6.1×10^{-4} emu/mol, 0.33 emu K/mol and -5.3 K, respectively. According to a simple fermi liquid theory, there is a simple relation between χ_P and γ:

$$\chi_P = \frac{3\mu_B^2}{\pi^2 k_B^2}\gamma. \tag{4}$$

The obtained value of χ_P is about 10% of that estimated from the value of $\gamma = 324$ mJ/mol K^2, 4.0×10^{-3} emu/mol. Any way, the value of χ_P is large and this is considered to be originated from the electrons with enhanced mass. The effective magnetic moment μ_{eff} is 1.62 μ_B and smaller than that of Ce^{3+} free ion. This indicates that strongly localized 4f electrons of Ce ion giving trivalency is rather limited (∼64%) in this compound. However, there also exists itinerant character with enhanced mass. At present, there is no comprehensive explanation of specific heat, electric and magnetic properties.

4. Conclusion

In CeOCuS, Ce ions exist in a mixed valence state. The upturn is observed in the temperature dependence of the specific heat. The electronic specific heat coefficient has a large value which is comparable with conventional heavy fermion compounds. The results of electrical resistivity and magnetization measurements support a heavy fermion like behavior. However, as no upturn and saturation are not observed in electrical resisitivity and magnetization measurements, respectively, the experiments at further low temperature are needed in order to confirm whether CeOCuS is really a heavy fermion compound or not.

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