

Transport properties of the spinel superconductor CuRh_2S_4 under pressure

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We have carried out the specific heat and electric resistivity measurements of the chalcogenide-spinel compound CuRh_2S_4 under the hydrostatic pressures up to 8.0 GPa, and found out the pressure induced superconductor-insulator (SI) transition at P_{SI} in between 5.0 and 5.6 GPa. The value of superconducting transition temperature T_c , which is 4.7 K at ambient pressure, increases up to 6.4 K at 4.0 GPa and turns to decrease with pressurization. With further pressurization, the abrupt loss of T_c occurs at P_{SI} and the system becomes an insulator. © 2005 American Institute of Physics. [DOI: 10.1063/1.1854251]

I. INTRODUCTION

The appearance of unusual physical properties on the chalcogenide-spinel compounds with general formula AB_2X_4 , such as the magnetic ordering,¹ the metal-insulator transition,^{2,3} and superconductivity,⁴ attract considerable interest and have potential of the technological applications. The chalcogenide-spinel compounds have the normal-spinel structure (space group $Fd\bar{3}m$) where the A and B cations occupy the tetrahedral and octahedral sites surrounded by the X anions, respectively. The ternary spinel compounds CuRh_2S_4 and CuRh_2Se_4 show superconductivity at $T_c=4.7$ and 3.5 K, respectively.⁴ In contrast, CuIr_2S_4 has a metal-insulator transition at 226 K due to the unusual charge ordering,³ although the value of the lattice constant a of CuIr_2S_4 ($a=9.847$ Å) is between that of CuRh_2S_4 (9.787 Å) and of CuRh_2Se_4 (10.269 Å). This situation makes us imagine that compression gives rise to huge influence on transport properties of this system.

In this paper, we report that specific heat and electric resistivity of CuRh_2S_4 under the hydrostatic pressures, and by compression, CuRh_2S_4 changes abruptly from the superconductor to insulator at pressure between 5 and 6.5 GPa.

II. EXPERIMENT

The samples of polycrystalline CuRh_2S_4 were prepared by a direct solid-state reaction. The stoichiometric mixture of fine powders of Cu (99.999%), Rh (99.9%), and S (99.999%) was kept at 850 °C for 10 days in a sealed quartz tube. Then, the powder specimen was ground, pressed into the pellets, and sintered at 1000 °C for 3 days. All the processes of sample preparation were carried out in a glove box filled with purified argon to minimize oxidation of the pellet. The single-phase spinel structure of the samples was confirmed by powder x-ray diffraction method. Specific heat C_p measurement was carried out by a conventional adiabatic heat-

pulse method. Electric resistivity ρ was measured by a standard four-probe method in the temperature range between 4.2 and 300 K. A cubic anvil device was used for generating pressure up to 8.0 GPa.^{5,6}

III. RESULTS AND DISCUSSION

A. Specific heat and electric resistivity at ambient pressure

Figure 1 shows temperature dependence of specific heat divided by temperature $C_p(T)/T$ of CuRh_2S_4 as a function of T^2 . A jump in specific heat ΔC is observed at the superconducting transition temperature $T_c=4.6$ K. The low temperature part of specific heat in the normal state is well fitted by Debye T^3 law: $C_p(T)=\gamma T+\beta T^3$ as shown by the solid line in Fig. 1, where first and second terms are the contribution from electronic and lattice on the system, respectively. We estimated $\gamma=22.93$ mJ/K² mol and $\beta=1.00$ mJ/K⁴ mol, which

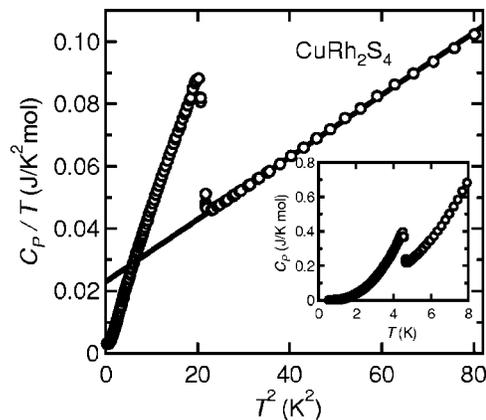


FIG. 1. Temperature dependence of specific heat divided by temperature C_p/T of CuRh_2S_4 as function of T^2 . The inset shows the plot of C_p as function of T .

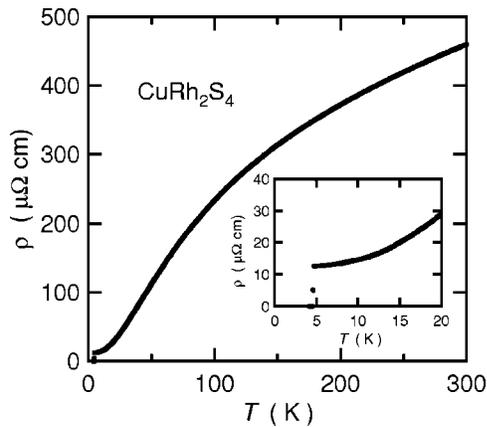


FIG. 2. Temperature dependence of electric resistivity $\rho(T)$ of CuRh_2S_4 between 4.2 and 300 K at ambient pressure. In the inset is expanded plot around T_c .

are close to the values reported by Hagino *et al.*⁴ From the value of β , we obtained the Debye temperature $\theta=239$ K by using the relation $\beta=12\pi nN_A k_B/5\theta^3$, where n is the number of the atoms per formula unit ($n=7$ in this system), N_A is Avogadro's number, and k_B is Boltzmann's constant. The normalized specific heat jump $\Delta C/\gamma T_c$ is 2.13 which is considerably larger than the BCS prediction of 1.43. Temperature dependence of electric resistivity $\rho(T)$ of CuRh_2S_4 between 4.2 and 300 K at ambient pressure is shown in Fig. 2. $\rho(T)$ shows metallic dependence defined as $\partial\rho(T)/\partial T > 0$ above $T_c=4.7$ K defined by the onset of the resistance drop. A residual resistivity at 4.8 K and residual resistance ratio are $12.6 \mu\Omega \text{ cm}$ and 36.5, respectively.

B. Electric resistivity under hydrostatic pressure

Figure 3 shows $\rho(T)$ at the various pressures. The variation of $\rho(T)$ above 3.0 GPa is complicated, although that is monotonic in low P range. A hump appears in $\rho(T)$ above 3.0 GPa at around T^* , which is indicated by arrows in Fig. 3. For $3.0 \leq P \leq 5.0$ GPa, with increasing pressure T^* decreases. The sign of $\partial\rho(T)/\partial T$ changes from negative to positive at T^* with decreasing temperature. As far as $\rho(T)$ shows a metallic T dependence, the superconducting transition occurs. In contrast, above 6.5 GPa, T^* increases with increasing

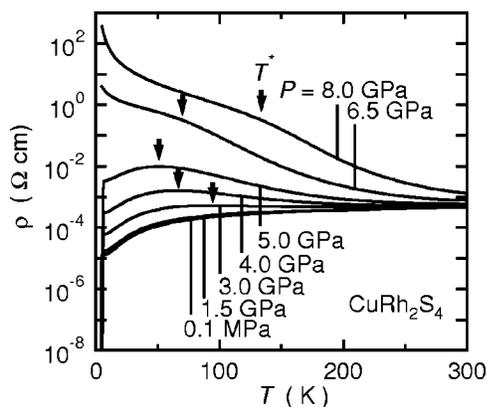


FIG. 3. The semilogarithmic plot of $\rho(T)$ at various pressures up to 8.0 GPa in the temperature range from 4.2 to 300 K. The arrows show the characteristic temperature T^* .

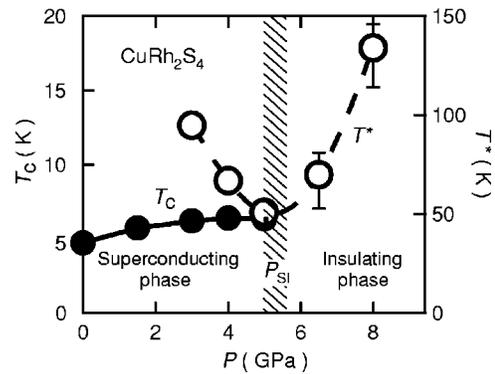


FIG. 4. T_c and T^* plotted as functions of P . The solid and broken lines are guides to the eyes. The phase boundary of pressure-induced superconductor-insulator transition is expected to lie at the hatched area.

pressure. $\rho(T)$ shows insulator T dependence defined as $\partial\rho(T)/\partial T < 0$ in whole temperature range and no trace of the T_c . The prominent feature of this data is the evolution of the $\rho(T)$ at low temperature range. The value at 10 K, for example, is enhanced by seven orders of magnitude due to pressurization from 0.1 MPa to 8 GPa. This pressure response is highly anomalous. Compression usually gives rise to reduction in resistivity in many materials and in some it gives rise even to superconductivity,^{7,8} because overlapping of electronic wave functions among neighboring atoms is promoted by compression.

The pressure dependences of T_c and T^* are shown in Fig. 4. The value of T_c increases with increasing pressure in lower pressure range as reported in a previous work carried out below 2 GPa,⁹ but that reaches a maximum value of 6.4 K at 4.0 GPa and then it starts to decrease. The abrupt loss of T_c occurs at P_{SI} in between 5.0 and 5.6 GPa where T^* has a minimum value, and the ground state of CuRh_2S_4 changes from superconducting to insulating. That is, pressure induced superconductor-insulator (SI) transition occurs at P_{SI} . We suppose the SI transition presumably results from the disappearance of carriers at the MI transition between 5.0 and 5.6 GPa. The mechanism of the MI transition is still unclear in the present case.

We discuss the two possibilities of MI transition at P_{SI} . One is due to the charge ordering of mixed valence Rh ion. The Rh ions, which occupy the octahedral sites (B sites), exist as Rh^{3+} electronic configuration of $4d^6 d\gamma^0$ and Rh^{4+} ($4d^5 d\gamma^0$) in the CuRh_2S_4 like the Ir ion exists as Ir^{3+} ($5d^6 d\gamma^0$) and Ir^{4+} ($5d^5 d\gamma^0$) in the isomorphous compound CuIr_2S_4 . Therefore, both the compounds have almost the same electronic structure. As the temperature decreases, CuIr_2S_4 shows a transition from a metal to an insulator at $T_{\text{MI}}=226$ K due to charge ordering of Ir^{3+} and Ir^{4+} , and a structural change occurs from cubic to triclinic symmetry with a volume contraction of 0.7%.³ This suggests that the triclinic insulator phase is preferred under pressure; indeed, it has been reported that T_{MI} increases by pressurization of CuIr_2S_4 .¹⁰ If we assume the same mechanism, CuRh_2S_4 , however, does not exhibit the MI transition at ambient pressure, and Rh^{3+} and Rh^{4+} charge ordering can be induced by pressure. In this case, the lattice changes from cubic to tetragonal by compression. Another possible origin, which is

not accompanied by a lattice change, is the modification of the band structure by compression. The fcc-Yb is known to be a material in which compression induces a semimetal-insulator transition without change of lattice symmetry.¹¹ The transition is ascribed to the formation of an energy gap between two bands, both of which originally cross the Fermi level in the semimetallic phase.¹² According to the study of band calculation for the CuRh₂S₄,¹³ the metallic conduction is due to the two holes per unit cell (two molecules) in the two branches which cross the Fermi level. Although CuRh₂S₄ is a good metal, an MI transition of the kind observed in the semimetal fcc-Yb may be expected if the two bands near the Fermi level are sensitive to pressure.

In order to clarify the mechanism of the pressure induced SI transition on CuRh₂S₄, it is important to investigate whether there is a structural change which is induced by compression. Although we have checked that there was no pressure-induced structural change in 300 K by the micro-Raman spectroscopy measurement under pressure up to 11.7 GPa,¹⁴ the crystal structure analysis under high pressure and low temperature is in progress.

IV. CONCLUSIONS

We have found a pressure induced SI transition in a chalcogenide-spinel CuRh₂S₄ from resistivity measurements under quasi hydrostatic pressure of up to 8.0 GPa. As pressure increases, the T_c value initially increases from 4.7 to 6.4 K and starts to slightly decrease after a broad maximum is reached. With further compression, supercon-

ductivity vanishes suddenly at P_{SI} around 5.3 GPa. The SI transition occurs in concurrence with a metal-insulator transition induced by pressure.

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