Electronic heat capacity of $CuIr_2Se_4$ at low temperature

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Abstract

The normal thiospinel $CuIr_2S_4$ exhibits a temperature-induced metal-insulator ($M-I$) transition around 230 K with structural transformation. A charge-ordering and spin-dimerization transition in $CuIr_2S_4$ has been found recently. In contrast to $CuIr_2S_4$, $CuIr_2Se_4$ remains metallic down to 0.4 K without the $M-I$ transition. The instability of the metallic state in $CuIr_2Se_4$ at high pressure has been previously reported. Heat capacity of $CuIr_2Se_4$ has been now measured over the temperature range of 0.5 to 11 K. The fit of the heat capacity data to $C = \gamma T + \beta T^3$ is very good with $\gamma = 6.68$ mJ mol-f.u.$^{-1}$ K^{-2} and $\beta = 4.09$ mJ mol-f.u.$^{-1}$ K^{-4}, where γT is the electronic heat capacity.

Key words: $CuIr_2Se_4$; electronic heat capacity; Debye temperature; metal-insulator transition

1. Introduction

Temperature-induced metal-insulator ($M-I$) transition occurs in a thiospinel $CuIr_2S_4$ around 230 K with structural transformation [1–9]. Simultaneously $CuIr_2S_4$ undergoes a charge-ordering and spin-dimerization transition [10]. With decreasing temperature, the magnetic state changes from the Pauli paramagnetism in high temperature metallic state to diamagnetism due to the atomic core orbital in the insulating state.

On the other hand, $CuIr_2Se_4$ remains metallic down to 0.4 K without the $M-I$ transition [2]. The pressure induced $M-I$ transition and the instability of the metallic state in $CuIr_2Se_4$ at high pressure have been investigated [11,12]. No trace of the structural transformation was observed up to 5 GPa. Heat capacity of $CuIr_2Se_4$ at ambient pressure has been measured over the temperature range of 0.5 to 11 K. Measurement of the heat capacity will provide insight into the nature of metallic state and the driving force behind the $M-I$ transition of $CuIr_2S_4$. Data of the electronic and lattice contributions to the heat capacity of $CuIr_2Se_4$ can be written as $C = \gamma T + \beta T^3$.

2. Experimental methods

The polycrystalline specimens were prepared by a direct solid-state reaction. Mixtures of high-purity fine powders of Cu (purity 99.99 %), Ir (99.99 %), Se (99.999 %) with an excess 0.1 wt% Se were heated in sealed quartz tubes to 1123 K and kept at this temperature for 10 days. The resultant powder specimens were reground and pressed to rectangular bars and then were heated to 1123 K for 2 days. The heat capacity measurement was made using a standard heat-pulse technique in the ^{3}He cryostat down to 0.5 K.

3. Results and discussion

Powder x-ray diffraction pattern at room temperature confirms that $CuIr_2Se_4$ has the normal-spinel type

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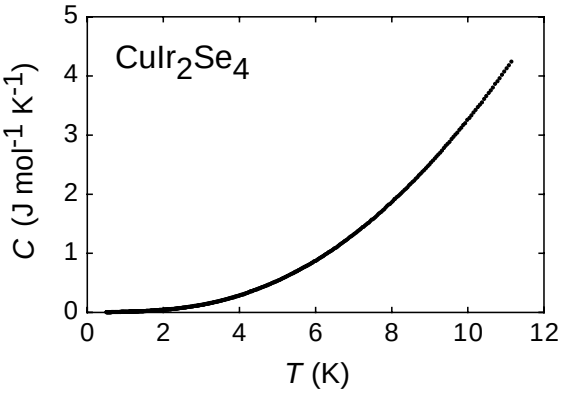

Fig. 1. Molar heat capacity of $CuIr_2Se_4$ over the temperature range of 0.5 to 11 K.

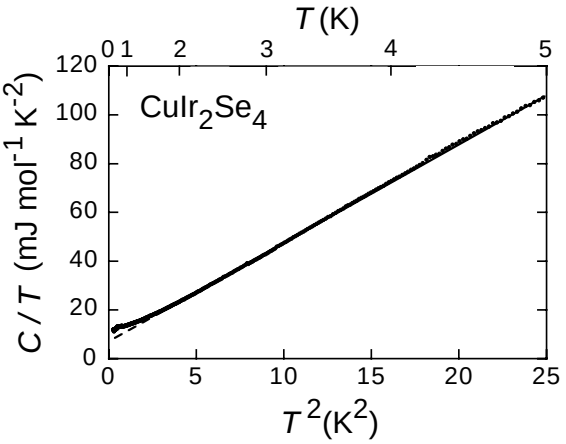

Fig. 2. Heat capacity for $CuIr_2Se_4$, plotted as C/T versus T^2. The broken line represents the heat capacity as calculated from $C/T = \gamma + \beta T^2$.

structure. The values of lattice constant a and u parameter are $a = 10.324$ Å and $u = 0.385$ for $CuIr_2Se_4$ at room temperature.

The temperature dependence of the molar heat capacity of $CuIr_2Se_4$ is shown in Fig. 1. Fig. 2 shows the molar heat capacity plotted as C/T vs T^2. No transition was observed in the heat capacity and the magnetic property down to 0.5 K for $CuIr_2Se_4$. The fit of the heat capacity data to $C = \gamma T + \beta T^3$ is very good with $\gamma = 6.68$ mJ mol-f.u.$^{-1}$ K^{-2} and $\beta = 4.09$ mJ mol-f.u.$^{-1}$ K^{-4}, where γT is the electronic heat capacity. The magnitude of γ is low, which indicates not to be heavy electrons. The small electronic contribution to the heat capacity suggests the less importance of electron-electron interactions. This result supports indirectly that the driving force of the $M - I$ transition in $CuIr_2S_4$ originates mainly from electron-phonon interactions. Below 1.0 K, there is small excess heat capacity over the calculated value from $\gamma T + \beta T^3$, which may arise from other origins. The heat capacity extrapolated over the entire temperature range is also shown as the broken line in Fig. 2 which is the result of a least-squares fitting of the data.

The Sommerfeld parameter for the electronic heat capacity, γ, is given as $\gamma = (1/3)\pi^2 k_B^2 D(\varepsilon_F)$, where $D(\varepsilon_F)$ is the band-structure density of state at Fermi level (for both spin direction). The value of $D(\varepsilon_F)$ is found to be 0.405 states eV^{-1} atom^{-1} for $CuIr_2Se_4$. The value of β for the Debye T^3 approximation for phonon is expressed as $\beta = (12/5)\pi^4 r N_A k_B \Theta^{-3}$, here the number of atoms per formula-unit, r, is 7 for $CuIr_2Se_4$. The Debye temperature Θ is obtained to be 149 K for the value of $r = 7$.

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