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Pressure effect on the superconductivity and the metal–insulator transition in $Cu_{1-x}Zn_xIr_2S_4$

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Abstract

The variations of the superconducting transition temperature T_c and the metal–insulator (MI) transition temperature T_{MI} were investigated as a function of pressure in the superconducting $Cu_{1-x}Zn_xIr_2S_4$ ($0.3 \leqslant x \leqslant 0.5$) system. The experiment was performed by measuring the temperature dependence of resistance under the pressures up to 1.5 GPa. It is shown that the external pressure destroys the superconductivity, and gives rise to the MI transitions. The result is discussed in terms of the stabilization of the insulating phase at high pressures and the phase separation associated with the charge segregation. It is proposed that the BCS Cooper pairs compete with the proposed bipolarons under certain pressures.

1. Introduction

Thiospinel $CuIr_2S_4$ shows an anomalous metal–insulator (MI) transition accompanied by a structural phase transition around 220 K in decreasing temperature [1]. With applying pressures, the MI transition temperature T_{MI} surprisingly *increases* [2], in contrast with the conventional behaviour. Recently, we found that Zn substitution for Cu suppressed the MI transition, and induced superconductivity at about 3 K when Zn concentration was higher than 22.5% [3–5]. Therefore, it would be interesting to study the pressure effect on the MI transition and the superconductivity in $Cu_{1-x}Zn_xIr_2S_4$ system.

2. Experiments

Powder samples of $Cu_{1-x}Zn_xIr_2S_4$ were synthesized by the chemical reaction of individual elements in a sealed quartz tube [3]. To prepare a densified pellet, the powdered sample was fired at 1223 K for 0.5 h under 6 GPa. After such a treatment, the phase decomposition of the

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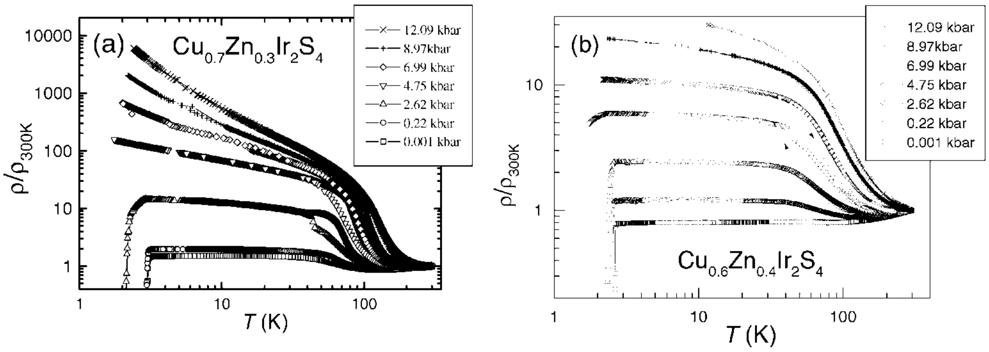

Figure 1. Temperature dependence of normalized resistivity at various pressures for $Cu_{1-x}Zn_xIr_2S_4$. (a) $x = 0.3$; (b) $x = 0.4$. Note that both the axes are in the logarithmic scale.

sample was clarified by the x-ray diffraction measurements. So, it is necessary to do further solid-state reaction at 1123 K in the sealed quartz tube so as to obtain the spinel single phase.

The resistivity was measured by employing dc four-probe method (down to 1.7 K). The pressure, which was generated by a piston–cylinder clamped cell with the liquid Fluorinert as the medium, was calibrated by measuring the superconducting transition temperatures of high-purity metal tin. The calibrated pressure at low temperatures (about 3 K) was about 60% of the loaded one at room temperature.

3. Results and discussion

Figure 1 shows the temperature dependence of resistivity for the dense $Cu_{1-x}Zn_xIr_2S_4$ samples at the ambient pressure. The superconducting transitions are obvious for the three samples. The superconducting transition temperature T_c decreases with increasing Zn content, consistent with the previous result [3, 5]. Sample of $x = 0.3$ shows an upturn in decreasing temperature at about 60 K with a small thermal hysteresis. Here we define this temperature as T_{MI}, which gives a point of inflection in the $\rho(T)$ curve. This is because that small amount of insulating phase is segregated below T_{MI} [4, 6]. In other word, both the cubic metallic phase and the non-cubic insulating one co-exist at low temperatures. As for $x = 0.4$ and 0.5, no sign is displayed to show the existence of the insulating phase at low temperatures.

Figure 1 shows the results of electrical resistivity measurement for the sample $Cu_{1-x}Zn_xIr_2S_4$ under various pressures. In figure 1(a), one can see that the superconductivity of $x = 0.3$ sample is seriously depressed, as indicated from the sharp decrease of T_c and the broadening of the superconducting transition. Under higher pressures, the resistivity upturn is enhanced very much, and the upturn-temperature ($\sim T_{MI}$) also increases with increasing pressure. The thermal hysteresis becomes obvious around 4 kbar, but it tends to vanish by the further pressurizing. Since the thermal hysteresis is directly connected with the first-order structural transition, the disappearance of the hysteresis suggests the change of MI transition from the first order into a higher order. In the case of $x = 0.4$ and 0.5, similar trends of the changes can be observed as shown in figures 1(b), though the details are different. The high-pressure semiconducting phase should have a cubic spinel structure, like that of the high-temperature metallic phase, because the structural phase transition is not probable as stated above, and the existence of the band gap is also questionable. Thus we called it quasi-semiconducting phase.

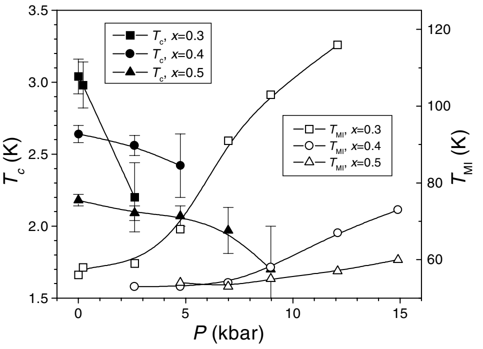

Figure 2. T_c and T_{MI} as a function of pressure in $Cu_{1-x}Zn_xIr_2S_4$. The T_c value is based on the superconducting midpoint temperature. The error bar denotes the transition width. T_{MI} is determined by finding a minimum dR/dT in the $T - dR/dT$ plot for heating process.

The pressure dependence of T_c and T_{MI} is concluded in figure 2. It is clear that T_c decreases, and superconducting transition width ΔT_c increases with increasing pressures. On the contrary, T_{MI} goes up monotonically by the pressurizing. The T_c changes are sharp for $x = 0.3$, but mild in the case of $x = 0.5$. Similarly, the $x = 0.3$ sample shows pronounced increase of T_{MI}, while the $x = 0.5$ sample has very small increase in T_{MI}.

Before discussing the above result, we shall talk about the background of the problem. First, we should remember it in mind that the Cu valence is +1 in the thiospinel system [3, 5–7]. The metallic non-doped $CuIr_2S_4$ phase is hole-conducted with the hole-concentration per unit formula, $n_h = 1$, as suggested by the band calculation [7]. The ionic configuration of the insulating $CuIr_2S_4$ phase, which is stable at high pressure [2], is most probably Cu^{1+} Ir^{3+} Ir^{4+} ${S_4}^{2-}$. Second, Zn substitution for Cu serves as a hole filling for the metallic phase [4, 5]. So, n_h becomes $(1 - x)$ for $Cu_{1-x}Zn_xIr_2S_4$. In the system with $0.1 \leqslant x \leqslant 0.3$, the coexistence of the two phases at low temperature was confirmed by x-ray diffraction analysis [4, 5]. The very recent Cu-NMR study suggested that the electronic state of the non-cubic insulating phase is hardly changed with the Zn-doping [6]. Namely, n_h of the insulating phase is almost kept to be 1.0 due to the electronic charge segregation, while n_h of the remaining metallic phase is less than the uniform hole concentration, $1 - x$. Third, we had shown that T_c decreased almost linearly with increasing Zn content from 0.3 to 0.7 [5]. In other word, T_c decreases with decreasing the hole-concentration.

Based upon the above description, the pressure effect can be phenomenologically understood in terms of stabilization of insulating phase and phase separation associated with the charge segregations. The stabilization of the insulating phase comprises of two aspects. The first is that T_{MI} is increased by the external pressures. The second is that the volume fraction of the insulating phase at low temperatures increases with increasing pressures. As stated above, the increase of the insulating phase results in the decrease of the hole-concentration of the metallic phase due to the charge segregations. Therefore, the applied pressure decreases T_c obviously.

The increase of the volume fraction of the insulating phase is consistent with the broadening of the superconducting transition. The increase of the insulating phase fraction also accounts for the rapid increase of low-temperature resistance due to the pressure. Note that the charge segregation results in a charge-aggregated states, which is after all not stable. Therefore, under certain pressure the charge aggregation collapses, and a uniform semiconducting phase forms. This explains that fact that the thermal hysteresis connected with the structural phase transition disappears under high pressures.

So, one may expect that an electronic state transition instead of the structural phase transition takes place under relatively high pressures. To explain the quasi-semiconducting behaviour for the cubic phase, bipolarons formation [5] is possibly involved. If so, the system would exhibit a transition from BCS Cooper pairs to bipolarons due to the applied pressures. How the two kind of pairs transform each other will be a very interesting issue in condensed matter physics. We expect some more detailed investigations on this point.

4. Conclusion

The temperature dependence of resistance for the densified $\mathrm{Cu}_{1-x}\mathrm{Zn}_x\mathrm{Ir}_2\mathrm{S}_4$ ($0.3 \leqslant x \leqslant 0.5$) samples was measured under the pressures up to 1.5 GPa. It was shown that superconductivity was suppressed, and the MI transition was recovered or changed by the external pressures. Under the relatively high pressures, no thermal hysteresis can be observable at the MI transition, implying that the transition belongs to an electronic state transition. The result is discussed in terms of phase separation associated with charge segregation. Bipolaron gas state is proposed for the cubic quasi-semiconducting phase.

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