Structural and Transport Properties of CuIr$_2$(S,Se)$_4$ under High Pressure


*Department of Science, University of Tsukuba, Tsukuba 305, Japan

**Department of Materials Science and Engineering, Muroran Institute of Technology, Muroran, Hokkaido 050, Japan

++ Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

The structural and transport properties of CuIr$_2$(S$_{1-x}$Se$_x$)$_4$ spinel compounds under high pressure have been studied up to 10 GPa. Resistivities of all samples were found to become insulating with increasing pressure even for the samples behaving metallic at ambient condition. When pressure was applied to the metallic samples with $x=0.9$ and 1.0, an anomalous peak appeared below 100K in the temperature dependence of the resistivity at lower pressure, but the semiconducting behaviour governed the whole temperature region at higher pressure. No structural change was observed at the temperature above and below the anomalous peak. This behaviour was discussed by the model based on some ordering of the localized charges induced by applied pressure.

1. Introduction

Recently it was discovered that there is a transition from metallic to insulating at 230K in CuIr$_2$S$_4$ [1]. The metallic phase appears in higher temperature region and the resistivity shows a discontinuous change at the metal-insulator (M-I) transition. An activation energy of 47 meV was obtained in the temperature range from 140K to 200 K. Accompanied with the transition, a structural transition from the cubic to the tetragonal lattice was also observed [2]. The volume of the metallic cubic phase at higher temperature becomes smaller by 0.7% at the transition to the insulting tetragonal phase. The results imply that the metallic phase becomes unstable for the volume contraction at high pressure. The X-ray diffraction pattern in the insulating phase at ambient pressure has been refined by a Rietveld analysis assuming a tetragonal structure with the space group $14_{1}$/amd. However, there are some weak reflections that cannot be explained by the assumed structure. It seems to indicate the existence of some superstructure originated from small atomic displacements. In addition, it was found that a magnetic transition occurs from paramagnetic in the metallic phase to diamagnetic in the insulating phase [2,3].

According to NMR [4] and XPS [5] measurements, the Cu ion is shown to be in monovalent state. Therefore, the mean valence of the Ir ion is concluded to be +3.5; that is, the number of 5$d$ electrons is 5.5. The band calculation of CuIr$_2$S$_4$ based on the local density approximation [6] shows the $d_{x^2-y^2}$ splitting in the Ir 5$d$ band, but the Fermi level lying near the top of the valence band (mainly the hybridized band of Ir 4$d$ and S 3$p$). The metallic behavior is thought due to one hole in the band with partial filling of 5.5/Ir atom. However the band structure can not predict the insulating phase resulting from the Fermi surface nesting by the modulation of electronic state. Although recent UPS measurement gives the consistent result for the metallic state with the band calculation, the gap opening is observed obviously in the insulating phase and explained probably due to electron correlation in spite of the general belief of weak correlation in S$d$-electron systems [5].

With the substitution of Se for S, a metallic phase is generally stabilized for the chalcogenides in spite of a volume expansion. In CuIr$_2$(S$_{1-x}$Se$_x$)$_4$, in fact, (i) for $x<0.2$, both the M-I transition temperature and the discontinuous change in resistivity at the transition decrease with an increase in $x$, (ii) for 0.2<$x$<0.8, the resistivity loses a jump-like change and becomes semiconducting in the whole temperature range, and (iii) finally, it becomes metallic for $x>0.8$. With respect to the volume change, the Se-substitution conflicts with externally applied pressure, which is generally believed to stabilize the metallic state. It is therefore very interesting to know what happens under pressure when $x$ is increased and what kind of mechanism is dominant in the M-I transition of the CuIr$_2$(S,Se)$_4$ system at high pressure.

2. Experimental

Polycrystalline samples were prepared by a solid-state reaction method using the mixtures of Cu, Ir, S and Se elements with their stoichiometric ratio. The mixture was heated to 850°C and kept at this temperature for 10 days in a sealed quartz ampule. Synthesized powder was sintered at 850°C to sample for the resistivity measurements. Sample for X-ray diffraction was prepared from the sintered material.

The electrical resistivity of CuIr$_2$(S,Se)$_4$ was measured with the DC four-probe method using the cubic anvil apparatus operated up to 10 GPa as a function of temperature. Fluorinert liquid was used as the pressure medium. The gasket with a
Teflon inner cell is made of the mixture of amorphous boron and epoxy. We also carried out the in-situ X-ray experiment up to 10 GPa at low temperature for CuIr$_2$Se$_4$ sample. The resistivity was measured using a cubic-anvil type of high pressure apparatus in connection with an X-ray diffraction system employing a rotary target type X-ray source and an energy dispersive detector. Low temperatures down to 7 K were attained by a continuous flow of liquid helium and nitrogen.

3. Results

The pressure dependence of the electrical resistivity for CuIr$_2$(S$_{1-x}$Se$_x$)$_4$ at room temperature is shown in Fig.1. From these results, it has been found that the instability of metallic phase is associated with a volume decrease at high pressure. In fact, the M-I transition of CuIr$_2$S$_4$ is obviously observed to initiate above 2 GPa. Because of the broad transition in the resistivity, it is difficult to estimate the pressure coefficient $dT_M/dP$ correctly, but roughly it was obtained to be 0.2-0.3K/GPa. These results are in agreement with the previous works [2, 7]. The insulating phase is stable up to 10 GPa, that is the maximum pressure in the present work. For CuIr$_2$(S$_{1-x}$Se$_x$)$_4$ as $x$ increased, the critical pressure becomes unclear.

However, the increment of the electrical resistivity with increasing pressure is retained for every sample, as shown in Fig. 1. Even in CuIr$_2$Se$_4$ ($x=1.0$), which is metallic at ambient pressure, the electrical resistivity also increases with increasing pressure at room temperature.

Figure 2 shows the temperature dependence of the electrical resistivity for CuIr$_2$Se$_4$ at various pressures. As shown in Fig. 2(a), an anomalous hump appears at about 100K with increasing pressure. When the pressure is increased to 2.8 GPa, the anomaly becomes huge: the resistivity coefficient is positive for lower temperature, and then negative for higher temperature. When the pressure is further increased, as shown in Fig.2 (b), in which the electrical resistivity is plotted as a log scale, the anomalous peak disappears gradually because of the increase in the electrical resistivity at the lower temperature. As a result, semiconducting behavior is observed in the whole temperature range. Above 4 GPa, the temperature coefficients of the resistance are obtained to be negative in the measured temperature. This result suggests that the insulating phase becomes also stable with increasing pressure for CuIr$_2$Se$_4$.

In order to know whether or not the structure change is associated with the change in the electrical resistivity, in situ X-ray diffraction measurement at 2.8 GPa was carried out, at which the pronounced behaviour in the resistivity was observed. As shown in Fig.3, no structural phase transition was observed.
4. Discussion

The mean valence of Ir ions in CuIr$_2$S$_4$ is thought to be +3.5. Thus the valence states in the insulating phase might be localized and separated into Ir$^{3+}$ and Ir$^{4+}$ with the equal weight, that is, Cu$^{1+}$Ir$^{3+}$Ir$^{4+}$S$^{2-}$. If the Ir ions are in low spin state, an Ir$^{3+}$ ion is in non-magnetic and an Ir$^{4+}$ ion has a local moment of $S=1/2$. Therefore, the diamagnetic property in the insulating phase indicated from the magnetic susceptibility$^2$ is interpreted as the formation of Ir$^{4+}$ dimers. This might be consistent with the observation of some superstructure spots in the X-ray diffraction for the insulating phase. The origin of the M-I transition may be closely related to the charge ordering at the Ir sites, which induces the dimer of Ir$^{4+}$. Similar situation of the valence state seems to occur in the insulating state stabilized by the volume contraction at high pressure in the whole system of CuIr$_2$(S,Se)$_4$.

CuIr$_2$(S,Se)$_4$ is a normal spinel with the space group $Fdar{3}m$. It is formed by a nearly close-packed fcc array of anions with holes partly filled by the cations. The copper atoms in the A site are tetrahedrally surrounded by the anions and the iridium atoms in the B site are octahedrally surrounded by anions. In this spinel structure, there is only one variable positional parameter $u$ for S or Se.

In a series of thiospinel, CuIr$_2$S$_4$ ($T$=Ti, Cr, V, Co), when the lattice constant decreases, the positional parameter $u$ is given to increase gradually$^8$. At high pressure, the lattice constant is also decreased by applied pressure. So the positional parameter $u$ should be increased. For the spinel structure, this means, certain rotation of the IrX$_6$ ($X$=S,Se) octahedron occurs for the relaxation of the volume contraction. That is, the increase of the $u$-parameter causes the enhancement of tilting of neighboring octahedrons relaxing the volume contraction. Presumably the localization of charge, i.e. the separation of valence state for Ir ions in the B sites, is accompanying with above process. Also the transfer integral between the Ir 5$d$-orbitals is expected to become small due to the tilting enhanced by pressure. Finally the applied pressure leads the gap opening in the top of the valence band, for example, due to the splitting of 5$d^5$ states for Ir$^{4+}$ from the valence band.

It is very interesting that the instability of metallic phase is induced at high pressure for this spinel system. To understand these phenomena, further studies are necessary, such as more accurate experiments of the structure, the hole coefficient, the specific heat measurement at high pressure and so on. The authors acknowledge helpful discussions with Dr. T. Sasaki.

References