The chalcogenide spinel, $CuIr_2S_4$, under high pressure

Alka.B.Garg [1], V.Vijayakumar[1], B.K.Godwal[1], Hans. D. Hocheimer [2]
[1]High Pressure Physics Division, Bhabha Atomic Research Center, Mumbai 400085, India. [2] Physics Department of Physics Colorado State University Fort Collins, CO 80523, USA.
Email:vvijay@apsara.barc.ernet.in

INTRODUCTION

Several transition metal chalcogenides exhibit mixed valence (MV) and a variety of phenomena like structural transitions (ST), insulator- metal transitions (IM), and charge, magnetic and superconducting (T_c) ordering. Among these compounds CuT_2X_4 (T=Rh,Ir, X=S,Se) are being recently investigated, mainly because of the interplay between superconductivity, the ionic state of Rh and Ir, and an unusual low temperature insulating phase stabilized by doping, pressure, or low temperature. The compound $CuIr_2S_4$ has spinel structure at room temperature. In this cubic structure, Cu ions are tetrahedrally and Ir ions octahedrally coordinated with the S atoms. At ambient temperature, the Ir ion is intermediate valent (3.5**)** exhibiting metallic behavior characterized by a rather low value of σ = 102 S/cm [Andreev.V.N., 2002]. It exhibits a metal to insulator transition when cooled below 230K [Nagata S., 1994]. Low temperature x-ray diffraction measurements show that the metal insulator transition is accompanied by structural transition from the cubic to a triclini**c** phase with a 0.7% reduction in volume [Furubayashi T**.** ,1994 & Radaelli P.G.,2004]. Recent band structure calculations [Betsuyaku K., 2004] have revealed the instability of the high temperature cubic phase. The authors found saddle points with 24 fold degeneracy near the Fermi energy, and they concluded that the triclinic distortion stabilizes the electronic state by lifting the degeneracy. Magnetic susceptibility measurements showed that the insulating phase do not have any localized spins [Furubayashi T**.** ,1994]. In the ionic model evoked to explain this unusual low temperature behavior, a MV configuration for Ir ($Cu^{+1}Ir^{+3}Ir^{+4}S^{-2}{}_4$) is postulated. Structural investigations of the insulating phase further indicate that there is charge ordering of two anions Ir^{+3} and Ir^{+4} along with Ir^{+4} dimerization [Radaelli P.G**.**,2004]. The dimerization of Ir^{+4} (spin =1/2) to a state S=0 state is needed to account for the magnetic data. $CuIr_2S_4$ is the only example of a three dimensional structure with charge ordering and spin dimerization [Radaelli P.G**.**,2004]. Further, x-ray irradiation disorders the dimerized lattice and induces a triclinic to tetragonal structural transition in which the electrical resistivity is reduced by a factor of 10^3 [Ishibashi.H, 2002]. The original state can be restored by thermal annealing, but even in the tetragonal state, the triclinic structure is preserved locally.

Magnetic susceptibility and electrical resistance measurements under pressure show that the MI transition temperature increase with increasing pressure [Furubayashi T**.** ,1994 &Oomi.G, 1994]. This is contrary to the case of most oxides that exhibit MI transitions [Adler D., 1968] where the metallic phase is stabilized by pressure. Thus the structural and transport properties of this material exhibit interesting features. Here we report the results of electrical resistance (R) and x-ray powder diffraction measurements on $CuIr_2S_4$ under pressure at ambient temperature .

EXPERIMENTAL

The sample was prepared by heating stoichiometric mixture of powders of Cu, Ir and S (99.99% purity) with a 1% excess S. The mixture was vacuum-sealed in quartz tubes and heated at 850^{o}C for 10 days. The material was characterized by x-ray powder diffraction to be of single phase having spinel structure (a=9.851Å). A clamp type diamond anvil cell with diamond anvils of culet size of 400 μm was employed for the measurements of the electrical resistance. A stainless steel gasket with a 400 μm hole**,** stuffed with alumina (Al_2O_3) powder with 0.05μm grain size**,** is used as sample cell. During the pre-compaction of the alumina powder, a thin mylar sheet (thickness 2 μm) is also put over the alumina powder. This reduces the pressure gradient in the sample substantially [Garg.A.B, 2004]. Two 19 μm stainless steel wires centered on the other anvil serve as leads for four probe measurements. The part of the wires over the anvil face is flattened using a tungsten carbide pin to avoid the shifting of wires when the load is applied. Fine powder of ruby, filled between the wires, is used to measure the pressure**,** and also ensures that the wires do not short within the anvil face area. The sample in the form a thin plate is placed so that it crosses the wires. By adjusting the lead layout and the sample size, the measurements are restricted to a small segment of the sample (40 μm length) in the center of the diamond. It ensures that the effect of pressure inhomogeneities is minimized. Before each measurement, the resistance between the leads and the gasket is measured to check for the shortening of leads with the gasket. Full details are given elsewhere [Garg.A.B, 2004].

The ADXRD measurements were carried out at the X ray diffraction beam line of Elettra synchrotron source at Trieste, Italy. The X-rays are monochromatized by a double silicon crystal monochromator. The beam is collimated to 80 μm diameter employing tungsten pinholes. A 345 mm image plate (IP) area detector from Mar Research is employed for recording the diffraction image. The image was recorded with 88x88 μm spatial resolution. The x-ray wavelength and sample to IP distance was calibrated by collecting ADXRD data for silicon and LaB_6. Fine particles of the sample were loaded into a hardened stainless steel gasket hole of 100 μm diameter along with silver as internal pressure marker. Ethanol was used as the pressure-transmitting medium. Prior to loading the sample, the cell with an empty gasket was fixed in a computer controlled X-Y-Z stage and aligned in the X- ray beam. The data were collected with a typical exposure time of 15 -30 minutes for each pressure point depending on the beam intensity. Two-dimensional data thus obtained are converted to standard one-dimensional pattern using FIT2D software [Hammersley A.P**.**, 1996]. X-ray measurements under pressure were carried out up to 30 GPa.

DISCUSSION

The results of the electrical resistance measurements are shown in Fig 1. The resistance increases gradually and around 15 GPa reaches a value that is approximately forty times the initial value. Beyond 15 GPa the resistance decreases up to 32 GPa and at 35 GPa, it tends to saturate at a value slightly above the ambient pressure value.

The evolution of x-ray diffraction patterns with pressure is shown in Fig 2. The cubic phase is stable only up to 1.3 GPa corresponding to a compression of 0.8%. The volume decrease at the cubic to triclinic structural transition is of the same order (0.7%). The powder pattern collected at 2.5 GPa shows a splitting of some reflections. For example, the [111] reflection in th**e** spinel structure splits into three components indicating a structural distortion (Fig 2&3). Since the [111] reflection in the spinel

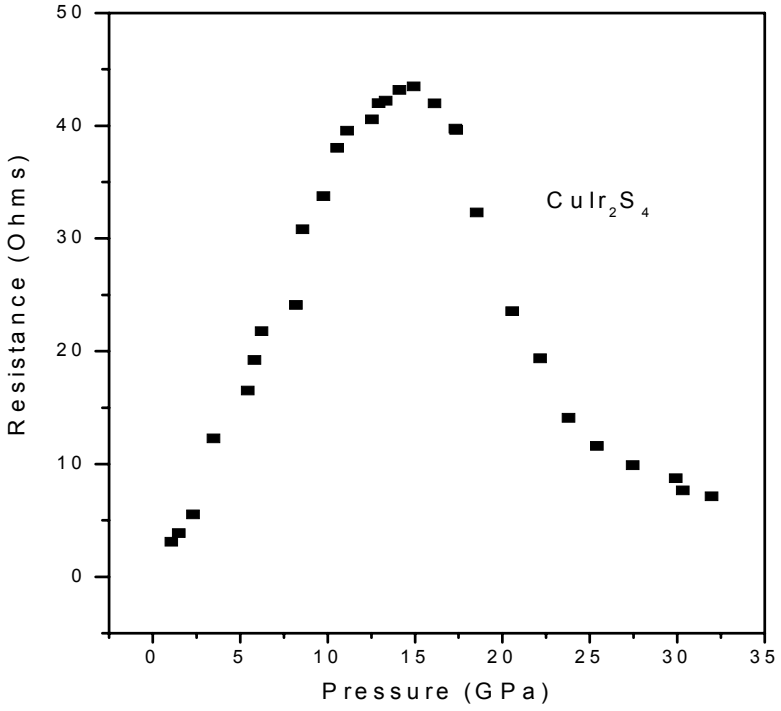

Fig. 1 Variation of the electrical resistance with pressure.

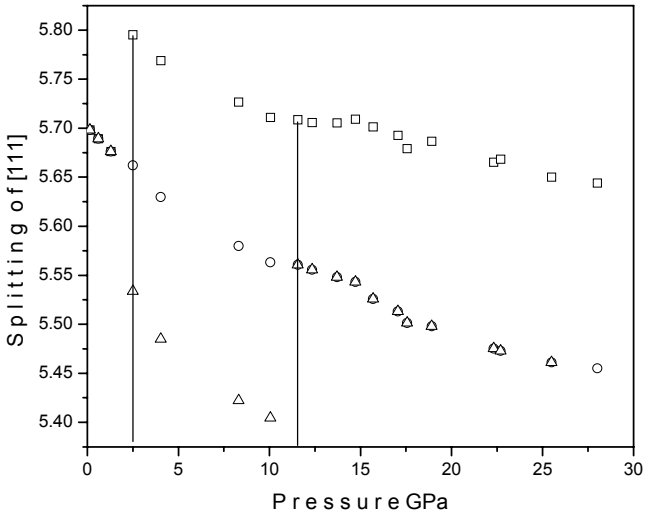

Fig. 2 Splitting of the [111] reflection in the spinel structure with pressure. Vertical lines are drawn to indicate pressures at which there is a change in splitting.

structure splits into three, it is obvious that the high pressure phase is different from the low temperature phase. In the low temperature phase it splits only into two. It is reasonable to assume that the pressure induced splitting of the reflections is also associated with some structural distortion. We are still working to determine the nature of

this distortion. However, as shown in fig 3a&b, where the change in splitting of the [111] reflection with pressure is shown, the distortion increases with pressure

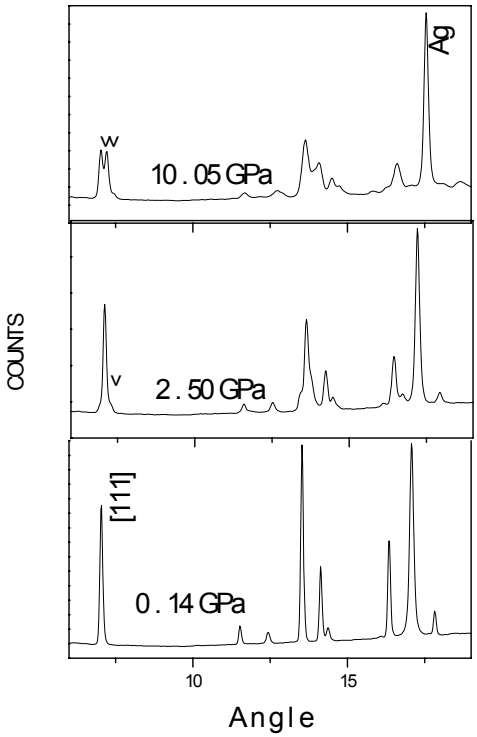

Fig 3a. Pressure evolution of the diffraction patterns. Only the low angle region is shown to make the splitting visible

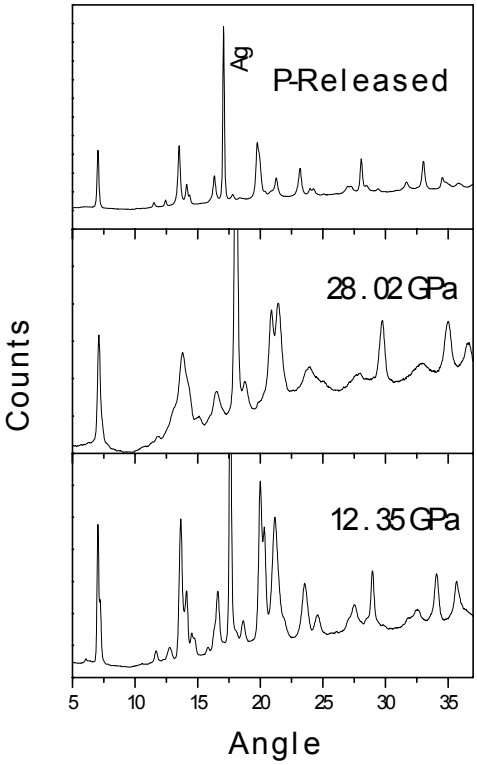

Fig3b Pressure evolution of the diffraction pattern above 12 GPa. The pattern exhibits line broadening.

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above 14GPa, we observe a gradual broadening and reduced splitting of the reflections. Thus the increase in electrical resistance with pressure correlates with the structural distortion with the highest resistance observed at the largest distortion. The increase in resistance with distortion is consistent with a variable range hopping model of conduction. As the distortion increases, the available equivalent sites reduce. Another interesting aspect is that the reflections start to broaden (as compared to Ag reflections) above 12 GPa indicating a pressure induced disorder. However, the ambient phase is recovered when the pressure is released.

CONCLUSION

$CuIr_2S_4$ undergoes a pressure induced structural transition above 1.3 GPa. There is a close correlation between the variation of electrical resistance and the structural transition with pressure. Above 28 GPa, $CuIr_2S_4$ has a reentrant metallic phase. It will be interesting to investigate whether this phase will exhibit superconductivity.

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