THE D.C. VOLTAGE-DEPENDENT RESISTIVITY OF CuCl POWDER COMPACTS UNDER PRESSURE

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The CuCl powder compacts are found to exhibit d.c. voltage dependent resistivity. The resistivity drops by six orders of magnitude when the applied voltage exceeds a critical value $V_c$. $V_c$ is found to decrease with the increase in pressure. The high conducting phase shows a positive temperature coefficient of resistance at 1 atm of 0.004°C⁻¹ which increases with pressure at a rate of $0.00045°C^{-1}GPa^{-1}$. It is suggested that the pressure induced transition reported at 4 GPa could arise from the application of d.c. voltage.

In this paper the d.c. voltage—current characteristics of CuCl powder compacts at atmospheric and higher pressures are reported. The resistance of the sample is found to be voltage dependent and exhibits a nearly six orders of magnitude drop when voltage above a critical value is applied across the sample. The temperature coefficient of resistance in the conducting phase has been also measured.

The CuCl samples were prepared [1] by heating at 80°C for 1 hr, 8 g of analytical grade CuCl₂ in 50 ml of high purity vacuum distilled glycerol. The major impurities in CuCl₂ were as follows: SO₄, Fe, Ni < 0.01%; Ba < 0.005%; alkalis and other metals as sulphates < 0.1%. The CuCl precipitate was filtered, washed with ethanol and dried in vacuum. The resulting white polycrystalline powder was heated at 200°C in a quartz tube, which was continuously evacuated to remove traces of glycerol and ethanol. The tube was then sealed and maintained at 450°C for 3 days. The vapour of CuCl condensed in the cooler region of the tube. The condensate was removed, sealed in a fresh quartz tube and the process was repeated. The vapour deposited powder was preserved in dark under dry nitrogen atmosphere. The X-ray diffraction patterns confirmed that the sample was CuCl with zinc blende structure and no other phase was present.

The experimental arrangement [2], used to measure the resistance of the sample at atmospheric pressure, consisted of a teflon cylinder (13 mm long, 3.5 mm i.d. and 5 mm o.d.) containing a pyrophyllite cube (cube edge 13 mm). The sample sandwiched between two upper electrodes (3 mm dia., 0.1 mm thick) was placed inside the teflon cylinder. The remaining space was filled by two pyrophyllite plugs (3 mm dia., 6 mm thick). The sample assembly was pressurised at 0.2 GPa in a cubic press [2]. The resistance measurements were made after unloading the sample assembly. The measurements at high pressures were carried out with a tungsten carbide opposed anvil set-up.

The resistance of the sample was measured by applying a known d.c. voltage and measuring the resulting current. The voltage was increased in steps of 80 mV. After each voltage increase, a waiting period of 1 min was allowed before noting the readings. In the conducting phase the resistance was measured by passing 10 mA d.c. current through the sample and measuring the resulting voltage.

The plot of log $(R/R_i)$ against applied voltage $V$ at different pressures ($R_i$ is the initial resistance of the sample) is shown in Fig. 1. It is observed that the resistance of the sample decreases with the increase in voltage and at a critical voltage $V_c$ it drops by nearly six orders of magnitude. In the conducting phase the resistance becomes independent of the applied voltage. The specific resistance of the conducting phase is nearly 50 kΩ cm, as compared to $10^7 Ω$ cm of the starting material. It is seen from Fig. 1 that $V_c$ tends to decrease with increase in pressure. Similar results were obtained with platinum electrodes.

In similar experiments with a.c. voltage across the sample, the resistance was observed to be independent of the applied voltage and the conducting phase was not observed.

The temperature coefficient of resistance $\alpha$ in the conducting phase was measured at various pressures by heating the anvils to nearly 60°C (room temperature 27°C). It was observed that $\alpha$ was positive with a value of $0.004°C^{-1}$ at one atmosphere. This value of $\alpha$ is close to those for metals. Further, $\alpha$ increased with increase in pressure at a rate of $0.0004°C^{-1}GPa^{-1}$. The standard deviation in $\alpha$ was found to be 0.0002 in each run. However, the values of $\alpha$ from two different runs at the same pressure differed by as much as five times the standard deviation.
The resistivity of CuCl powder compacts under pressure was almost instantaneous, however, the recovery time was more than 3 days for a sample which was maintained in the conducting phase and the pressure of the sample regains the original resistance on disconnecting the power supply, it may be necessary to postulate a disproportionation reaction which is reverse of eqn. (1). However, a disproportionation reaction is hard to visualise if the free copper is in the form of precipitates. Alternatively, the disproportionant CuCl can be thought of as a system wherein segregating copper atoms occupy octahedral sites and an electron from a small region of segregating copper creates a virtual exciton across the boundary to the charge ordered state. The freed copper, according to Blount and Phillips [4], is in the form of Guinier–Preston transitional precipitate, and gives rise to the high conducting phase [5]. The temperature coefficient of resistance of the conducting phase has a value close to that for metals and lends an indirect support to this explanation. Since the sample regains the original resistance on disconnecting the power supply, it may be necessary to postulate a disproportionation reaction which is reverse of eqn. (1). However, a disproportionation reaction is hard to visualise if the free copper is in the form of precipitates. Additionally, the disproportionant CuCl can be thought of as a system wherein segregating copper atoms occupy octahedral sites and an electron from a small region of segregating copper creates a virtual exciton across the boundary to the charge ordered state [3]. Clearly, a successful theory should explain the reversible nature of the conducting phase and the positive \( \alpha \).

The decrease in \( V_c \) with increase in pressure indicates a higher tendency for disproportionation at higher pressure, if it is assumed that the conducting phase arises because of disproportionation. The pressure dependence of \( V_c \) may arise from two distinct sources: one is the true pressure effect and the other is the plastic deformation caused when the sample is pressurised between the anvils. The line and the plane lattice defect produced during this plastic deformation may act as possible sites for the segregation of free copper when d.c. voltage is applied. Thus, the higher the pressure the larger will be the number of lattice defects. This can qualitatively explain the decrease in \( V_c \) with the increase in pressure.

The resistivity of CuCl has been reported to decrease by nearly six orders of magnitude at 4 GPa [5]; this was attributed to a pressure-induced transition. Since, the voltage-induced conducting phase also exhibits a resistance drop of similar magnitude in passing from the insulating to the conducting phase, it is tempting to make an attempt to explain the pressure-induced conducting phase as a transition triggered by the application of voltage. The typical currents passed through the sample to measure the resistance was nearly 1 \( \mu \)A [5]. Taking the resistance of the sample as \( 10^6 \Omega \), 1 V is required to pass 1 \( \mu \)A through the sample. It is seen from Fig. 1 that

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2\text{CuCl} \rightarrow \text{Cu} + \text{CuCl}_2. \tag{1}
\]
that at 4 GPa, \( V_e \) is nearly 0.8 V. Thus the voltage applied to measure the resistance could have caused a conducting phase in the experiments of Chu et al. [5]. However, it will remain unexplained. The value of the voltage-induced conducting phase is positive while it is negative [5] for the pressure induced conducting phase.

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Note added in proof: In experiments with \( \text{Cu}^{+}/\text{CuCl/Pt}^- \) cell, deposition of copper on Pt-electrode was observed when conducting phase was maintained for nearly 15 hr. This may be because the applied voltage exceeds the decomposition potential (0.77 V, L.G. Harrison and Mahendra Prasad, J. Chem. Soc. Faraday Transactions I, 471 (1974)) for the reaction \( 2\text{CuCl} \rightarrow \text{Cu} + \text{CuCl}_2 \). The conducting phase may arise from the formation of copper filaments by electrolysis.

REFERENCES