

LETTER TO THE EDITOR

CuCl

High pressure metallic phase in cuprous chloride single crystals

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Abstract. An insulator-metal-insulator sequence of transitions has been observed as a function of pressure in a freshly prepared single crystal of CuCl. The metallic phase is evidenced by a sudden drop in resistance by a factor of $\sim 10^7$ between ~ 40 Kbar and ~ 55 Kbar.

1. Introduction

Cuprous halides form tetrahedrally coordinated zinc blende structures and thus in some sense are related to the isoelectronic sequence of group IV elements, and III-V and II-VI semiconductors. However in many ways the cuprous halides are anomalous when compared to other members of the isoelectronic sequence. Martin (1970) has shown that the reduced bulk modulus of CuCl is only $\leq 20\%$ of that expected by extrapolation, and that the reduced shear moduli are also unexpectedly soft. Inelastic neutron scattering results (Carabatos *et al* 1971, Hennion *et al* 1972) show that the transverse acoustic branches are low and flat over most of the zone, and that there is an intermediate maximum in the longitudinal acoustic $|110|$ branch of CuCl. Extensive optical, ultraviolet and x ray photoemission data (Tono *et al* 1973, Goldman *et al* 1974) give evidence that the 3d levels in Cu are strongly hybridized into the valence band as might be anticipated solely from the structural dissimilarity of the cuprous halides and the alkali metal halides. In CuCl the upper branch of the valence band arises mainly from the 3d states (Tono *et al* 1973, Goldman *et al* 1974) of Γ_{15} symmetry and the spin-orbit splitting at the top of the valence band is inverted (Cardona 1963, Shindo *et al* 1965).

Increase of pressure causes covalent and moderately ionic 4-coordinated zinc blende structures to collapse to the (4 + 2)-coordinated white tin structure. Highly ionic zinc blende structures on the other hand collapse directly to the insulating 6-coordinated NaCl structure (Klement and Jayaraman 1966). Again the cuprous halides are anomalous in that many phases, (Edwards and Drickamer 1961, Van Valkenburg 1964, Rapoport and Pistorius 1968, Bradley *et al* 1969) as yet not well characterized, have been observed by a number of workers as a function of pressure below the melting curve. Van Valkenburg has

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observed that CuCl transforms to a birefringent phase that is opaque in transmitted white light.

The present experiments were motivated by the above results and their suggestion of the possibility of a highly-conducting high-pressure phase. Indeed, we have observed a sharp resistance drop in CuCl by a factor of $\sim 10^7$ at 40 kbar indicating the entering of a metallic phase before it transforms into a much less conducting phase at $P \gtrsim 55$ kbar.

2. Experimental details

Crystals were grown using the gel-growth process, (Armington and O'Connor 1967, 1968) because this process is capable of yielding large high-purity (Armington *et al* 1967) single crystals. The crystals were grown at 15°C to slow down the rate of growth and thus improve the purity and crystalline perfection (Hensch 1970). Powder pattern x ray analysis indicated that the crystals were single phase in the zinc blende structure. Clear tetrahedral crystals 1.0–2.5 mm on an edge were hand-picked for property measurement. Since the crystals tend to decompose to CuCl_2 and Cu on exposure to air (especially moist air), they were stored in a 1% HCl solution, a few Cu pellets being added to the solution to retard the $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$ reaction. A dry N_2 atmosphere was used whenever the crystals were removed from the solution for handling. The crystals were always handled and grown under dim red light to avoid light-induced deterioration. Isomica packing rings and AgCl or Teflon pressure medium were used with the Bridgeman anvil sets to provide the high-pressure environment at room temperature. Both Mo- and W-strips with Cu-coated contacts to the samples were used for leads. Crystals were ground down to 0.1–0.2 mm thick triangular platelets and loaded on to the anvil sets. The two-point resistance was measured by an HP 410B VTVM, and the pressure was calculated from the load determined by a calibrated Dutt–Norton gauge. Runs on one polycrystalline sample

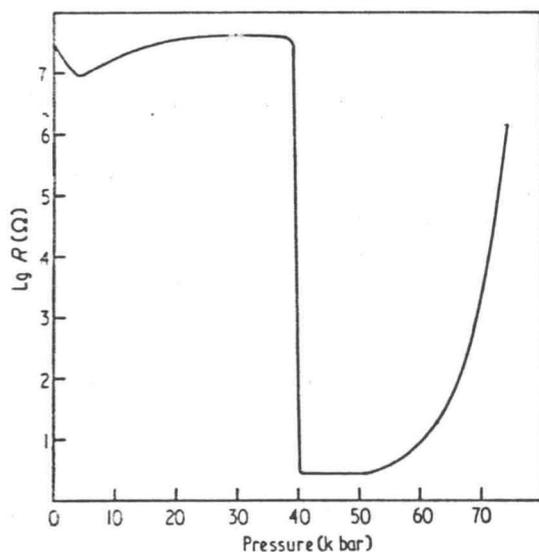


Figure 1. Schematic pressure dependence of resistance for a CuCl crystal at room temperature (300 K).

(prepared by melting and cooling at room temperature for $P \leq 20$ kbar).

Schematic results for the resistance R decreased initially and then increased only slightly (peaking at 40 kbar) with pressure up to 40 kbar. Below 40 kbar, $R \sim 30 \times 10^6 \Omega$ and $\sim 6 \times 10^6 \Omega$ through 40 kbar by ≤ 2 kbar. Further increase of pressure led to a sharp drop in resistance. However, for higher P , R increased again, $R \sim 75$ kbar.

It should be noted that the sharp drop in resistance was caused by pinching or shearing of the sample in only seven of them. We observed defects in the samples. Six of the samples were one semicircular crystal, which occurred in crystals prepared by the gel-growth process. We also noticed that the resistance increased with increasing pressure and decreasing pressure cycle change (or latent heat) according to the case of Sm-monochalcogenides over a 9 K range was also observed in one sample. As the pressure decreased, the resistance increased rapidly without significant hysteresis jump. The anomaly is absent in the other samples.

3. Conclusions

The results shown in figure 1 indicate a phase transition in CuCl at 40 kbar and a sharp drop in resistance at a transition at somewhat higher critical pressure required for the formation of a metallic phase. These observations are consistent with the fact that CuCl powder at high pressure near 40 kbar can easily form a metallic phase of CuCl particles and their aggregates.

Only tentative speculation is possible at this time although the transition from a covalent- to metallic- to collapsed metallic phase is suggested.

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(prepared by melting and cooling CuCl powder) were also carried out inductively at low temperature for $P \leq 20$ kbar by a self-clamp technique (Chu *et al* 1968).

Schematic results for one of the CuCl single crystals are shown in figure 1. The resistance R decreased initially (presumably due to improvement of contacts) and then increased only slightly (perhaps due to the freezing out of the defects) with increase of pressure up to 40 kbar. Beyond and close to this pressure, R started to oscillate between $\sim 30 \times 10^6 \Omega$ and $\sim 6 \times 10^3 \Omega$. After very slowly cycling the pressure back and forth through 40 kbar by ≤ 2 kbar, R eventually dropped to $\sim 3 \Omega$ including the contact resistance. Further increase of P to ~ 55 kbar did not induce any significant change in R . However, for higher P , R increased rapidly, finally reaching a value of $\sim 3 \times 10^6 \Omega$ at ~ 75 kbar.

It should be noted that not all runs were successful. Eighteen runs excluding those caused by pinching or shorting of leads were made, and large drops in R were detected in only seven of them. We attribute this to the chemically unstable nature of, and the defects in, the samples. Six out of the seven successful runs were made, with five clear and one semiclear crystal, within two weeks after preparation, while most of the failing runs occurred in crystals prepared more than five weeks prior to the run, or in semiclear crystals. We also noticed that violent explosions occurred at ~ 40 kbar in both increasing and decreasing pressure cycles for many cases. This may be attributed to the drastic volume change (or latent heat) accompanying the transformation into the metallic state similar to the case of Sm-monochalcogenides (Jayaraman 1971). A large AC susceptibility jump over a 9 K range was also detected around 85 K and at 20 kbar in the fused polycrystalline sample. As the pressure decreased, the size of the jump decreased and the width increased rapidly without significantly shifting the temperature of the midpoint of the susceptibility jump. The anomaly is absent at 1 bar.

3. Conclusions

The results shown in figure 1 and discussed above show there is an insulator-metal transition in CuCl at 40 kbar and room temperature which is then followed by a metal-insulator transition at somewhat higher pressure. Based on the preliminary susceptibility data, the critical pressure required to induce the transformation may decrease with temperature. These observations are consistent with previous electrical study of compressed and fused CuCl powder at high pressure by Bradley *et al* (1969). Their failure to detect large conductivity near 40 kbar can easily be attributed to the possible large contact resistance between CuCl particles and their experimental conditions.

Only tentative speculations as to the nature of the insulator-metal transitions are possible at this time although it seems possible they result from a progressive change from covalent- to metallic- to ionic-bonding. Detailed investigation of the nature of the CuCl collapsed metallic phase by a modified high pressure rig is in progress.

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LETTER TO

The absence of local hopping conduction

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