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TITLE: SOLID-STATE PHASE TRANSITIONS IN CuCl UNDER HYDROSTATIC PRESSURES TO 12.8 GPa

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The appearance of the "fishbone" pattern in the sample observed with this sample. Sharp and large crystalline regions reported in the literature and to be observed by them only in freshly prepared NaCl crystals appear to represent a special type of crystal growth, limited in the width and studied at distances of 10-15 μ m from the surface. Furthermore, it has been observed with the pure salt there is no transition to sharp lines in the x-ray light and as described the with other samples from the sample. Since the transition boundaries were easily seen in observed light a sequence of colored photos were taken with the sample between two crossed polarizers. While there is some background birefringence due to the diamonds, the crystal transition to isotropic is readily identified and seems to be completed to NaCl at less than 7 GPa.

Fig. 1. In this sequence CuI undergoes a phase transition at 4.3 GPa from the blende to tetragonal structure. These frames from a video recording system show (a) prior to transition at $P = 4.3$ GPa, (b-c) selected frames in a 1 sec period that show the progress of the phase transition, and (d) the completed transition to tetragonal phase at 4.7 GPa.

Disproportionation reactions have been discussed by Pinner and co-workers.¹¹ These reactions lead to the formation of elemental copper and only a small, order of one percent, amount of free copper would be left the visible part of the reaction. In a sealed sample several days to three weeks have been reported¹² as the time for detection of the opaque material. We have looked for the formation of the opaque material over a period of more than 10 weeks. As shown in Fig. 2 there is no indication of any opaque phase.

Additional information concerning possible disproportionation was obtained from a filled gasket cell.¹¹ The cell was held at 1.5×10^{10} GPa for ten weeks without visible change. At the reduced pressure of 5.0×10^9 GPa and a hold period of three weeks no visible change was observed, nor was there indication of an opaque phase forming during a four week hold at 1.5×10^9 GPa just above the lower transition. In our gasketed samples the higher pressure portion of the gasket edge so that disproportionation could be expected around the periphery. Since CuI is quite soft it is shown by the fact of only the resonance peak frequency.¹³ The pressure gradient in this sealed sample was not large enough to stimulate the disproportionation reaction. In comparison to the uniaxial cell results where disproportionation is clearly seen we conclude that significant pressure gradients are required to stimulate this reaction to free copper.

Although we have probed the sensitivity of the pure CuI to detect low level interaction with free copper no evidence has been found in any of the experiments. We have not ruled out the cell for this purpose although the power level of the cell is significantly reduced to 50×10^9 GPa by the optical filter. This contrasts with the observations in bulk samples which were prepared with an older technique showed strong coloration sensitively.

In summary, we have shown that copper iodide has a sharp transition as true of helium fluid has a sharp transition from the simple blende to the tetragonal structure at 4.3×10^9 GPa in agreement with earlier quasi-hydrostatic studies. These measurements were made with an cell prepared to assure high purity and near stoichiometry. The upper transition was observed at lower pressures but is difficult to observe in the

present experiment. No evidence is found for the formation of the opaque phase that would indicate a disproportionation to free copper. This observation agrees with the recently expressed idea that pressure gradients are required to drive this reaction.⁵

Fig. 2. A single video frame taken 10 μ sec after the CuCl₂ crystallite in helium bath was held at $P = 11.0$ kbar (10Pa). No evidence for free copper is observed by a reduction of the transmission.

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