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Polymorphism of Cuprous Iodide at High Pressure

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High pressure polymorphism of cuprous iodide has recently been a subject of wide interest. However, the results have been rather conflicting and the available X-ray data (1 to 3) are apparently in total disagreement. We have studied high pressure phases of CuI using an opposed diamond anvil type apparatus up to 80 kbar and 250 °C. The X-ray data to 60 kbar are rather similar to those reported by Moore et al. (3) the most important differences being the following: We index the phase stable above 15 kbar as hexagonal with $a = 4.13 \text{ \AA}$, $c = 20.35 \text{ \AA}$ at 27 kbar, 100 °C. The noncubic symmetry is supported by the observed birefringence (4) of this phase. The next transition, located by Moore et al. at 53 kbar, we find at substantially lower pressure suggesting that it is actually the same as that reported by Edwards and Drickamer (5) at 41 kbar. The difference is probably due to the sluggishness of this transition at room temperature. The data reported by Hinze (2) below 15 kbar appears to be assignable to a substantially higher pressure range.

Little information has been so far available of the behaviour of CuI in the region above 60 kbar. Van Valkenburg (4) extended his optical observations up to 125 kbar, but he did not report any transitions above 15 kbar. Edwards and Drickamer (5) detected a phase transition at 80 kbar by studying the optical absorption edge, while Moore et al. (3) did not find it in their resistivity data. All these studies have been performed at room temperature only. We wish to report evidence of a first order phase transition at 75 kbar, above 100 °C.

The phase stable above 60 kbar is a cubic superstructure of the zero pressure zb phase with doubling of the unit cell edge (3). At room temperature we have obtained smooth compressibility data, but after prolonged heating ($\approx 100 \text{ h}$) around 100 °C or a shorter high temperature treatment above 200 °C at pressures higher than 75 kbar we observe a volume discontinuity of about 2%. We have not detected any superstructure reflexions from the new phase, the X-ray pattern being other-

Table 1

X-ray diffraction data for CuI at 81 kbar, $a_0 = 5.631 \text{ \AA}$ (MoK α radiation)

hkl	$d_{\text{calc.}}$	$d_{\text{obs.}}$	$I_{\text{obs.}}$
100	5.631	5.61	w
(111) β	3.251	3.29	mw)
111	3.251	3.242	vs
200	2.815	2.813	mw
210	2.518	2.519	ms
211	2.299	2.271	m(d)
220	1.991	1.987	w
311	1.698	1.698	m

wise somewhat similar to that of the lower pressure phase. It is indexable to a primitive cubic unit cell with $a = 5.631 \text{ \AA}$ at 81 kbar as can be seen in Table 1. Due to the small number of the observed reflexions it is not possible to determine the structure unambiguously. However, it is of interest to note that it is not the predicted NaCl structure.

The volume compressibility in the high pressure region during typical runs has been presented in Fig. 1. The broken line indicates behaviour under decreasing pressure. It is probable that the slight discontinuity in the shift of the CuI absorption edge with pressure at 80 kbar (5) is associated with this same transition. It is to be noted, however, that the transition has not been observable in our room temper-

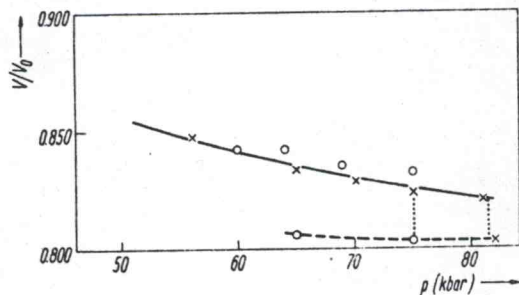


Fig. 1. X-ray data on volume compressibility of CuI at high pressure. Circles and crosses denote different runs, while the broken line indicates behaviour under decreasing pressure

$\lambda_0 = 5.631 \text{ \AA}$ (MoK α radiation)

	$I_{\text{obs.}}$
	w
	mw)
2	vs
3	mw
9	ms
1	m(d)
7	w
3	m

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ature data or in other work at room temperature.

As the behaviour of cuprous halides under high pressure appears very inter-
esting, we have continued these studies collecting recently X-ray data also on
high pressure phases of cuprous bromide.

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