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# High Pressure Phases of CuI†

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In addition to the 14-kbar transition in CuI reported by Bridgman, there have been reports of phase transitions at 4-kbar and 5-kbar on the basis of optical observations. X-ray diffraction results using a diamond anvil cell give no indication of any structural change up to 14-kbar. This transformation is very sluggish and is not completed until a pressure of about 30-kbar is attained. Furthermore, another phase transition, not previously reported occurs at approximately 53-kbar. These results have been verified by resistivity measurements in the belt apparatus. The structures of the two high-pressure phases have not yet been completely solved, but both of them appear to require unit cells that are supercells of the starting zincblende structure.

In 1932 P. W. Bridgman reported compressibility data for powdered specimens of CuI (*1*), and later, in 1937, reported a phase transition in CuI at about 14 kbar (*2*). This transition appeared as a discontinuous volume change with

$$\frac{\Delta V}{V_0} = 3.96\%$$

at 14.5 kbar. The variation in transition pressure with temperature was also studied and gave a linear dependence with

$$\frac{dT}{dP} = -0.0595°\mathrm{C/kbar}$$

between −100°C and +150°C. These early studies by Bridgman were done at moderate pressures, and in none of them did he reach 50 kbar.

Since this first work by Bridgman, many other investigators have reported phase transitions in CuI at high pressure. In 1963 Van Valkenburg (*3*) reported two new phase transitions on the basis of optical observations up to 125 kbar: one at 4 kbar, and another at 5 kbar. The 4-kbar phase was characterized as being birefringent, and the 5-kbar phase as isotropic. He also observed the phase reported by Bridgman and characterized it as being weakly birefringent.

Edwards and Drickamer (*4*) studied the effect of pressure on the absorption edge in CuI and reported two new phase transitions: one at 41 kbar, and another at 80 kbar. The 14-kbar transition reported by Bridgman was observed as a discontinuity in the shift of the absorption edge with pressure. Samples were studied to 150 kbar and no evidence for the transitions at 4 and 5 kbar was reported. Admittedly, the apparatus appears to be more sensitive to changes at higher pressures.

More recently, Neuhaus and Hinze (*5*) studied CuI up to 20 kbar. Using both optical and electrical resistivity measurements they claimed to see the 4- and 5-kbar transitions first reported by Van Valkenburg. They also report a volume change for the 14-kbar transition of 4.3% which is in fair agreement with Bridgman's value of 3.96%. No volume changes are given for the 4- and 5-kbar transitions.

Yang, Schwartz, and LaMori (*6*) have recently published the results of studies on high-pressure polymorphism in CuI. They also claim to see the 4- and 5-kbar transitions, as well as the 14-kbar transition reported by Bridgman. Samples were studied up to 28 kbar and 450°C, and from these data they were able to construct a *P-T* phase diagram.

We have been studying the diffraction patterns of CuI up to 60 kbar and at room temperature for some

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time using a modified Bassett diamond anvil cell (*7,8*), and find no evidence of first-order phase transitions below 14 kbar. The X-ray data, besides showing the 14-kbar transition, indicates another previously unreported phase transition at approximately 50 kbar. Furthermore, these findings seem to be corroborated by DC electrical resistance measurements in the belt apparatus, which show only the two phase transitions deduced from the X-ray observations (Fig. 1). In particular, no indications of transitions at 41 and 80 kbar as reported by Edwards and Drickamer are seen. The 14-kbar transition is quite sluggish and does not appear to be complete until well above 25 kbar, whereas the 53-kbar transition takes place more rapidly and appears complete at about 60 kbar. The resistivities for the two phases are found to be:

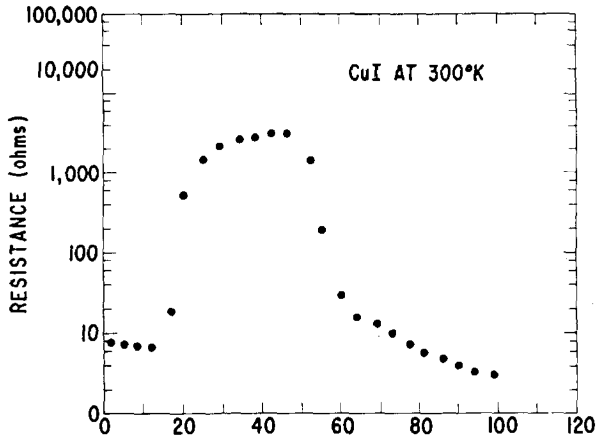


FIG. 1. Resistance vs. Pressure for CuI at room temperature.

$\rho_{14} = 164$ ohm·cm at 33 kbar

$\rho_{53} = 0.155$ ohm·cm at 55 kbar

The measured interplaner spacings for the two high-pressure phases as well as for the initial zincblende

TABLE I

CuI

X-RAY DIFFRACTION DATA

Ag K$\alpha$ RADIATION ($\lambda = 0.5608$ Å)

| *1 bar* $a_0 = 6.051$ Å | | | | *33 kbar* $a_0 = 11.627$ Å | | | | *55 kbar* $a_0 = 11.463$ Å | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *hkl* | $d_{calc}$ | $d_{obs}$ | $I_{obs}$ | *hkl* | $d_{calc}$ | $d_{obs}$ | $I_{obs}$ | *hkl* | $d_{calc}$ | $d_{obs}$ | $I_{obs}$ |
| | | | | 111 | 6.713 | 6.820 | w | | | | |
| | | | | | | | | 200 | 5.730 | 5.690 | vw |
| | | | | | | | | 311 | 3.460 | 3.50 | vw |
| 111 | 3.494 | 3.493 | s | 222 | 3.356 | 3.364 | s | 222 | 3.310 | 3.326 | s |
| 200 | 3.025 | 2.996 | w | 400 | 2.907 | 2.924 | w | 400 | 2.866 | 2.867 | w |
| | | | | 331 | 2.667 | 2.656 | m$^-$ | | | | |
| | | | | | | | | 420 | 2.563 | 2.554 | m |
| | | | | | | | | 422 | 2.340 | 2.341 | w$^-$ |
| | | | | 511,333 | 2.237 | 2.230 | m | 511,333 | 2.206 | 2.180 | w$^-$ |
| 220 | 2.139 | 2.144 | s | 440 | 2.055 | 2.059 | s | 440 | 2.027 | 2.027 | s |
| | | | | | | | | 600,422 | 1.911 | 1.909 | vvw |
| | | | | 533 | 1.773 | | | 533 | 1.748 | | |
| | | | | | | 1.763 | m$^+$ | | | 1.736 | m |
| 311 | 1.824 | 1.824 | w$^+$ | 622 | 1.753 | | | 622 | 1.728 | | |
| 400 | 1.513 | 1.517 | vw | 800 | 1.453 | 1.444 | vw | 800 | 1.433 | 1.436 | w |
| | | | | | | | | 820,644 | 1.390 | 1.387 | vw |
| 311 | 1.388 | | | 662 | 1.334 | 1.339 | w | 662 | 1.315 | 1.318 | w |
| | | 1.392 | w | | | | | | | | |
| 420 | 1.353 | | | | | | | | | | |
| 422 | 1.235 | 1.239 | w | 844 | 1.187 | 1.187 | w | 844 | 1.170 | 1.173 | w |
| | | | | | | | | 10·2·0,862 | 1.124 | | |
| | | | | | | | | | | 1.120 | w |
| 511,333 | 1.164 | 1.161 | vw | 10·2·2,666 | 1.119 | 1.129 | vw | 10·2·2,666 | 1.103 | | |
| 531 | 1.022 | 1.015 | vw | | | | | | | | |

phase are shown in Table I. The proposed indexing for both high-pressure phases is based on a supercell of a zincblende phase, i.e., a doubling of the cell edge. Although the new lines are weak they are quite easily reproducible. The fact that the strong zincblende lines persist seems to indicate that the basic cubic close packing of iodine atoms may be preserved, and that the structural changes at pressure result only from a redistribution of copper atoms among the available interstices. The exact nature of the distribution is still under investigation.

Recent work by Rapoport and Pistorius (*9*), employing DTA measurements at pressure, support the fact that there are no first order phase transitions at 4 and 5 kbar. However, we feel that the 41-kbar point shown on their *P-T* phase diagram should actually be at 53 kbar.

We are presently attempting to obtain more accurate intensity data to aid in solving the structure of the 14-kbar phase and also the new phase at 53 kbar.

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