

## High-pressure phase of copper(I) iodide

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The structural properties of copper(I) iodide have been investigated at pressures up to 40 GPa using the angle-dispersive x-ray diffraction technique with an image-plate area detector. A previously unreported structural phase transition is observed in the region of 17.3 to 18.2 GPa, from the antilitharge structured phase CuI-V (space group  $P4/nmm$ ) to an orthorhombic structure (space group  $Cmcm$ ). The latter has been labeled CuI-VIII and can be considered as a heavily distorted rocksalt arrangement, with the cation environment closer to fivefold coordination than regular octahedral. No evidence was found for the rocksalt structured phase observed at  $\sim 12$  GPa by previous workers.

At ambient conditions the three copper(I) halides CuCl, CuBr, and CuI all possess the cubic zinc-blende structure (space group  $F\bar{4}3m$ ). They represent the end members of a series of tetrahedrally coordinated semiconductors which comprise the group IV elements and the III-V, II-VI, and I-VII compounds. The bonding is purely covalent in the group IV elements but becomes increasingly ionic with increased separation of the constituent elements in the periodic table. However, the copper(I) halides are still not purely ionic, CuI having an ionicity of  $f_i = 0.692$  on the Phillips scale.<sup>1</sup> This is close to the critical value  $f_c = 0.785$  which marks the boundary between compounds characterized by fourfold coordination (zinc-blende structure) and those with sixfold coordination (rocksalt).

Static compression favors transitions to more densely packed structures, so the copper(I) halides might be expected to transform from zinc-blende to rocksalt under hydrostatic pressure. In a recent neutron diffraction study,<sup>2</sup> CuCl and CuBr were found to adopt the rocksalt structure (space group  $Fm\bar{3}m$ ) at pressures of 10.6(3) GPa and 7.4–9.3 GPa, respectively, though the zinc-blende  $\rightarrow$  rocksalt transition occurs via several intermediate structures of lower symmetry. In CuI, the zinc-blende phase (CuI-III) transforms to a rhombohedral structure (CuI-IV) at 1.63(1) GPa (Ref. 3) and then to a tetragonal phase (CuI-V) at 4.70(5) GPa.<sup>2</sup> The latter structure is anti that of litharge (red PbO) and is stable up to the highest pressure possible in that study<sup>2</sup> (9.69 GPa). In an earlier x-ray diffraction study,<sup>4</sup> Meisalo and Kalliomäki suggested that CuI adopts the rocksalt structure above  $\sim 10$  GPa. However, their experimental data are limited to a single diffraction measurement at 12 GPa made at ambient temperature after the sample had been heated to enhance the kinetics of the transformation. Four reflections were observed, of which only three are consistent with a rocksalt structure with  $a = 5.15$  Å. This paper presents the results of angle-dispersive x-ray diffraction measurements on CuI which examine and clarify the structural behavior of CuI above 10 GPa.

Commercially available CuI supplied by the Aldrich Chemical Company, of stated purity 99.999%, was used in this work. Finely ground material was loaded into diamond-anvil cells of the Merrill-Bassett<sup>5</sup> and Diacell<sup>6</sup> design, which allow diffraction data to be collected up to a maximum scat-

tering angle  $2\theta \sim 40^\circ$ . A 4:1 mixture of methanol:ethanol was included as a pressure-transmitting medium and the pressure measured using the ruby fluorescence method. The experiments were performed on station 9.1 at the Synchrotron Radiation Source, Daresbury Laboratory using the recently developed image plate setup,<sup>7</sup> with an incident wavelength  $\lambda = 0.4652(1)$  Å. Two-dimensional powder diffraction data collected on the image plates were read on a Molecular Dynamics 400A PhosphorImager and then integrated to provide one-dimensional diffraction patterns with the PLATYPUS program.<sup>8</sup> Least-squares refinements of the diffraction data were performed using the FULLPROF (Ref. 9) program.

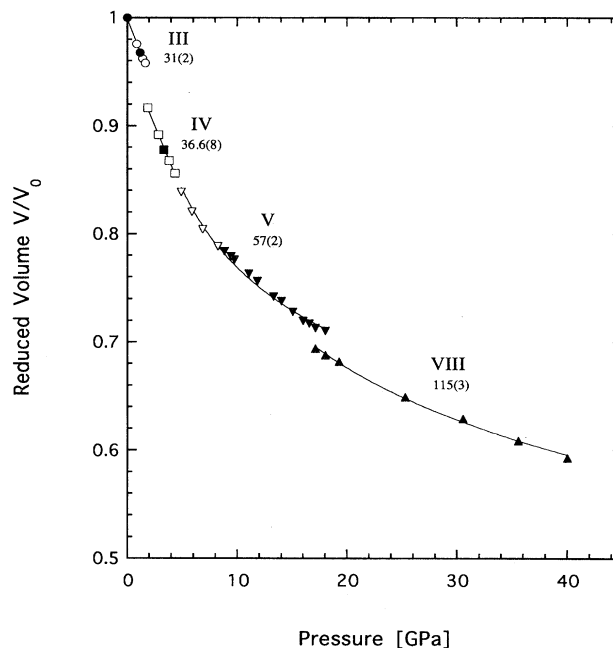


FIG. 1. The compressibility of CuI plotted as reduced volume ( $V/V_0$ ) versus pressure. The symbols denote the various phases as follows;  $\circ$  for CuI-III;  $\square$  for CuI-IV;  $\nabla$  for CuI-V, and  $\triangle$  for CuI-VIII. Filled symbols are from this work and open symbols are values from Refs. 2 and 3. The values next to each curve give the bulk modulus of each phase in units of GPa.

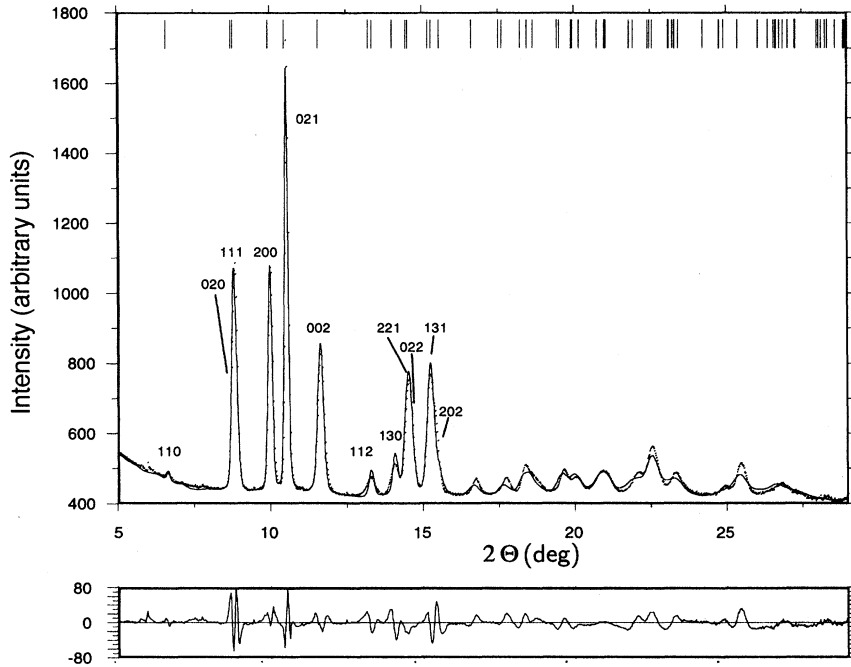


FIG. 2. Fit to the CuI profile collected at 19.2 GPa. The tick marks show the positions of all reflections allowed by symmetry (the first twelve indexed reflections are labeled). The difference between the observed and calculated pattern is shown slightly enlarged in the smaller box below.

In this experiment only limited data were collected below 8 GPa because this pressure range was extensively investigated in our previous neutron diffraction studies.<sup>2,3</sup> The tetragonal antilitharge phase (CuI-V) was found to be stable up to at least 18.2 GPa. No evidence of significant structural changes associated with a phase transition to the rocksalt phase found by Meisalo and Kalliomäki<sup>4</sup> at  $\sim 10$ –12 GPa could be detected. At 17.3 GPa additional reflections at 8.7°, 9.8°, and 10.4° were observed, in addition to the Bragg reflections of CuI-V. Both phases coexist up to  $\sim 18.2$  GPa but on increasing the pressure to 19.2 GPa all the lines associated with CuI-V had disappeared. The sample was then assumed to have completely transformed to the new phase, which remained stable up to the highest pressure achieved ( $\sim 40$  GPa).

Following the notation of Merrill,<sup>10</sup> this new phase is labeled CuI-VIII, though the transition pressure and its diffrac-

tion pattern do not agree with those observed previously by Meisalo and Kalliomäki.<sup>4</sup> Instead, the diffraction lines of phase CuI-VIII could be indexed using an orthorhombic unit cell having  $a = 5.35$  Å,  $b = 6.09$  Å, and  $c = 4.58$  Å. Density considerations indicate that the unit cell contains four CuI formula units. The compressibility of phase VIII is shown in Fig. 1 in the form of  $V/V_0$  versus pressure, where  $V_0$  is the unit-cell volume per formula unit at ambient pressure. Using the Birch equation<sup>11</sup> an estimate of  $B_0 = 115(3)$  GPa is obtained for the bulk modulus of CuI-VIII. The volume change at the transition CuI-V  $\rightarrow$  CuI-VIII is 2.3% calculated from a dataset collected at a pressure of 17.7 GPa where both phases are observed simultaneously.

The single-phase data collected at 19.2 GPa were used to determine the structure of CuI-VIII. Systematic absences were found for  $(hkl)$  reflections with  $h+k$  odd and for  $(h0l)$  with  $l$  odd. With the assumption of site ordering in the

TABLE I. Results of least-squares refinements of the diffraction data for CuI. X-ray data are from this study and previous neutron data (Ref. 2) are shown for comparison.  $B_{\text{Cu}}$  and  $B_{\text{I}}$  are the cation and anion isotropic thermal vibration parameters, respectively. The remaining symbols are described in the text.

	CuI-V <i>P4/nmm</i>			CuI-VIII <i>Cmcm</i>	
	Neutron	Cu in $(\frac{3}{4}, \frac{1}{4}, 0)$ , I in $(\frac{1}{4}, \frac{1}{4}, z_1)$ X ray	X ray	Cu in $(0, y_{\text{Cu}}, \frac{1}{4})$ , I in $(0, y_{\text{I}}, \frac{1}{4})$ X ray	X ray
Pressure [GPa]	5.55(2)	8.8(3)	16.7(2)	19.2(2)	30.8(3)
$a$ [Å]	4.0229(3)	3.9598(2)	3.8539(8)	5.3727(15)	5.1896(23)
$b$ [Å]				6.1154(17)	5.9263(28)
$c$ [Å]	5.6506(8)	5.5459(5)	5.3551(13)	4.6087(13)	4.5435(21)
$y_{\text{Cu}}$				0.6015(8)	0.5999(15)
$y_{\text{I}}$				0.1918(3)	0.1839(6)
$z_1$	0.2913(4)	0.2993(3)	0.3095(5)		
$B_{\text{Cu}}$ [Å <sup>2</sup> ]	1.32(5)	2.27(9)	3.79(15)	1.84(10)	1.49(14)
$B_{\text{I}}$ [Å <sup>2</sup> ]	0.75(3)	1.67(6)	1.71(7)	1.67(7)	1.21(10)

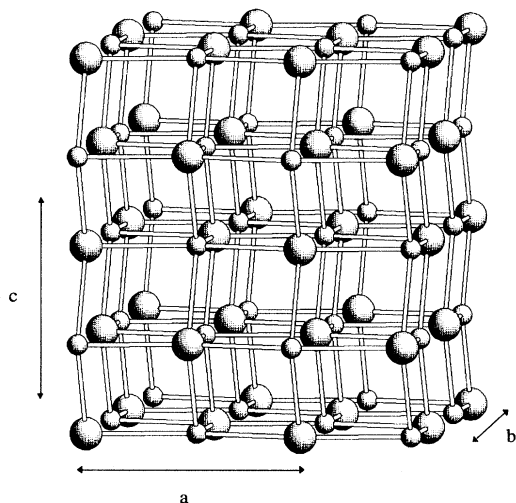


FIG. 3. The crystal structure of the orthorhombic  $Cmc2_1$  phase of CuI-VIII. The smaller spheres correspond to the copper ions.

CuI-VIII structure, the systematic absence conditions restrict possible space groups to  $Cmc2_1$ ,  $C2cm$ , and  $Cmc2_1$ . The two other possible  $C$ -centered spacegroups,  $C2cb$  and  $Cmca$ , are ruled out by the two weak reflections (110) and (130). Site ordering restrictions and the observed absences are, therefore, consistent with sites  $4c$  of  $Cmc2_1$ ,  $4b$  of  $C2cm$ , and  $4a$  of  $Cmc2_1$ . Initial Rietveld refinements were then carried out in the highest symmetry space group  $Cmcm$  by placing both  $I^-$  and  $Cu^+$  ions in the  $4c$  sites at  $(0, y, \frac{1}{4})$  with  $y_I \sim \frac{1}{8}$  and  $y_{Cu} \sim \frac{5}{8}$  to approximate the strength of the intensities of the reflections (200) and (021) and the relative weakness of the (020) reflection. The least-squares refinements confirmed this to be the correct structure, yielding values to  $y_I = 0.1918(3)$  and  $y_{Cu} = 0.6015(8)$ . It should be noted that the difference between the two  $y$  values ( $\sim 0.41$ ) is significantly different from the initial value of  $\frac{1}{2}$ , which corresponds to the rocksalt structure when  $a = b = c$ .

Analysis of the difference plots (observed-calculated profile) revealed the presence of anisotropic broadening effects for the  $(0kl)$  reflections with  $k$  odd. These are interpreted as particle size effects in the sample and were described using an additional parameter included in the fit. Preferred orientation effects were modeled assuming needlelike crystals with the crystallographic axis chosen initially to reduce the (200) reflection intensity and then iteratively optimized to fit the other affected reflections. However, severe preferred orientation effects were only observed in the mixed phase CuI-V + CuI-VIII region. The remaining variables included in the structure refinement were a scale factor, the three lattice parameters, two variable atomic coordinates  $y_I$  and  $y_{Cu}$ , two isotropic thermal motion parameters, and five peak-shape parameters. The resulting fit is shown in Fig. 2. The final unit cell and atomic parameters are listed in Table I, together with the values obtained for the tetragonal phase V for comparison. The few remaining misfits discernible in Fig. 2 result from the inability of the relatively simple one-parameter models to account for the size and preferred orientation effects. Similar effects have also been observed in related II-VI compounds.<sup>11,12</sup> Trial refinements were also carried out in the

lower symmetry space groups  $C2cm$  and  $Cmc2_1$ . However, these gave no significant improvement in the quality of the fit and we conclude that the correct space group is  $Cmcm$ .

The crystal structure of CuI-VIII at 19.2 GPa is shown in Fig. 3 viewed down the  $[010]$  axis to reveal the relationship to cubic rocksalt. The orthorhombic structure can be considered as a distortion of the rocksalt-type structure with alternate flat (001) rocksaltlike planes of atoms displaced approximately  $\pm 0.09b$  along the  $[010]$  axis. This produces a marked zigzag along  $[001]$  and a coordination quite different from rocksalt. Each  $Cu^+$  ion is surrounded by one unlike nearest neighbor at 2.520(7) Å, two at 2.614(3) Å, and two at 2.740(1) Å, resulting in an irregular fivefold coordination. The sixth unlike next-nearest neighbor is at 3.602(7) Å, considerably further than the two closest  $Cu^+-Cu^+$  contacts at 2.634(5) Å. The nearest  $I^-I^-$  contacts are at 3.299(2) Å. The structure is thus very similar to the high-pressure structures of CdTe-IV (Ref. 12) and ZnTe-III (Ref. 13) which have essentially the same coordination but somewhat different lattice parameters. There is no evidence that the  $Cmcm$  structure tends towards rocksalt with pressure, as might be expected on the basis of simple packing considerations. This would be manifest as an increasing similarity of the three orthorhombic lattice parameters and a tendency for the difference in positional parameters ( $y_{Cu} - y_I$ ) to approach the

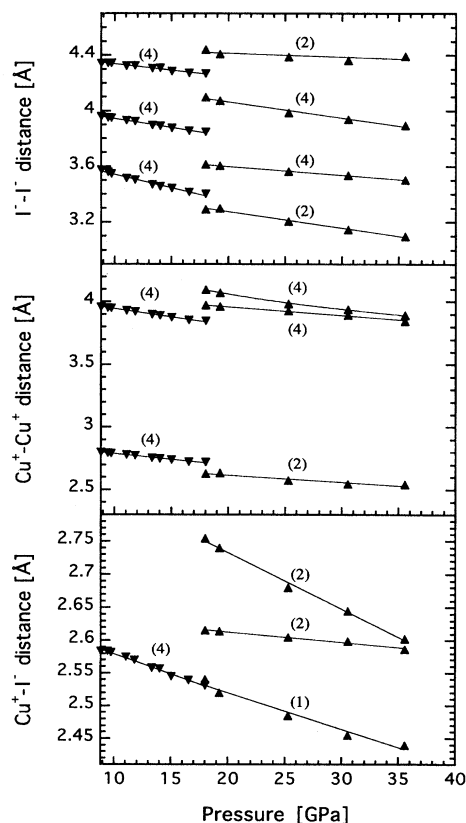


FIG. 4. The pressure variation of the bond length parameters for CuI above  $\sim 8$  GPa. The symbols are as follows: filled  $\nabla$  for CuI-V and filled  $\Delta$  for CuI-VIII. The values in parentheses give the number of equivalent contacts at that distance.

value  $\frac{1}{2}$ . Such behavior is not observed. As shown in Fig. 4, the most significant structural change with pressure in phase VIII is the increased similarity between the second and third nearest  $\text{Cu}^+ - \text{I}^-$  contacts and is a consequence of the relatively low compressibility of the  $c$  axis.

The pressure-induced phase transitions in CuI are from zinc-blende CuI-III ( $F\bar{4}3m$ )  $\rightarrow$  rhombohedral CuI-IV ( $R\bar{3}m$ )  $\rightarrow$  antilitharge CuI-V ( $P4/nmm$ )  $\rightarrow$  orthorhombic CuI-VIII ( $Cmcm$ ). The crystal structures of phases CuI-III, CuI-IV, and CuI-V can all be derived from an ideal cubic close-packed anion sublattice, in which the cations are fourfold coordinated but distributed in different ways over half the tetrahedral sites. In the simplest terms, such a redistribution of the cations within an ideal cubic close-packed lattice generates three structures with identical packing densities. The volume reduction with increasing pressure arises from increasing distortions in the anion sublattice through the sequence CuI-III  $\rightarrow$  CuI-IV  $\rightarrow$  CuI-V and has been discussed in more detail elsewhere.<sup>2</sup> The principal changes at the CuI-V  $\rightarrow$  CuI-VIII transition are a more significant distortion of the anion sublattice leading to four different anion-anion distances and a change in the anion environment around the cation from (distorted) tetrahedral to an irregular fivefold coordination.

The structural properties of CuI above 10 GPa have been

clarified using image plate diffraction data from a synchrotron x-ray source. No evidence for an octahedrally coordinated cubic rocksalt phase is observed up to  $\sim 40$  GPa. This finding is contrary to previous x-ray diffraction studies on CuI (Ref. 4) and to recent neutron diffraction studies which indicate the presence of rocksalt structured phases in CuCl and CuBr at  $\sim 10$  GPa.<sup>2</sup> A previously unreported pressure-induced phase transition is observed at 17.1 GPa, from the antilitharge phase CuI-V to phase VIII. The latter is found to be orthorhombic with a heavily distorted rocksalt arrangement in which the cation is in roughly fivefold coordination to the anion sublattice. Previous diffraction studies to pressures of  $\sim 10$  GPa (Ref. 2) suggested that the structural trends in the I-VII compounds were markedly different from the more covalent II-VI systems. This observation does not hold at higher pressures, since the crystal structure of CuI-VIII appears similar to the recently observed high-pressure structures of CdTe-IV (Ref. 12) and ZnTe-III.<sup>13</sup>

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