

## SHORT STRUCTURAL PAPERS

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## Structure of Cuprous Iodide, Polytype 12R

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**Abstract.** CuI, rhombohedral,  $R\bar{3}m$  (hexagonal axes given),  $a = 4.265$  (2),  $c = 41.96$  (1) Å,  $U = 661.0$  Å<sup>3</sup>,  $Z = 12$ ,  $M_r = 190.451$ ,  $D_c = 5.74$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 23.9$  mm<sup>-1</sup>,  $R = 0.033$  for 180 unique observed reflections. The structure consists of close-packed layers of I atoms on two crystallographically independent sites while the Cu atoms are disordered equally over four crystallographically independent sites comprising the tetrahedral holes between the iodine layers. The average Cu–I bond length is 2.616 (5) Å.

**Introduction.** Complexes between cuprous halides and tertiary phosphines and arsines have been extensively studied (Jardine, 1975). Some early work established the existence of complexes between cuprous halides and phosphine, which were unstable to loss of PH<sub>3</sub> (Scholder & Pattock, 1934; Holtje & Schlegel, 1940). We initially undertook to confirm the formation of CuI.nPH<sub>3</sub> complexes and to characterize them further by spectroscopic methods. In the process colourless, needle-like crystals of a polytype of CuI crystallized from PH<sub>3</sub>-saturated tetrahydrofuran solutions.

Polytypism according to Verma & Krishna (1966, pp. 61–191) may be defined in a general way as the ability of a substance to crystallize in different modifications in which two of the unit-cell dimensions usually remain the same while the third is a variable integral multiple of a common unit. The structures are thus considered to consist of layers parallel to the two invariant unit-cell axes and the polytypes are differentiated by their stacking sequences. Polytypism has been extensively observed in silicon carbide and zinc sulphide, and to a lesser degree in some other binary compounds. It is not surprising therefore that

CuI should also exhibit this phenomenon since it possesses, in its different phases, structures similar to those of the known phases of ZnS. Other than the phases known as  $\alpha$ -,  $\beta$ - and  $\gamma$ -CuI, only one polytype (6H) has been detected by diffraction methods (Kurdyumova & Baranova, 1961). This latter polytype was reported to have significantly greater conductivity than  $\gamma$ -CuI as do the high-temperature phases of CuI. These higher-conducting phases are thought to be ionic conductors of the  $p$  type. In this regard, detailed structural information of the different forms of CuI is of interest, particularly the distribution and thermal parameters of the Cu<sup>+</sup> ions as these parameters may reflect the mobility of the cations.

Intensity measurements were made at ambient temperature on a Syntex P2<sub>1</sub> diffractometer using graphite-monochromatized Mo  $K\alpha$  radiation. A cylindrical crystal (radius = 0.033 mm, length = 0.22 mm, cylinder axis = [100] hexagonal axis) was selected. Lattice parameters were calculated from 15 well-centred reflections with  $19^\circ \leq 2\theta \leq 28^\circ$  using Mo  $K\alpha_1$  radiation ( $\lambda = 0.70926$  Å). In the hexagonal-axis system reflections were systematically absent unless  $-h + k + l = 3n$ , indicating rhombohedral symmetry.  $R3m$  and  $R\bar{3}m$  were considered as possible space groups for a close-packed structure, but only the latter space group gave a satisfactory refinement. Intensities of reflections in the range  $0 < 2\theta < 55^\circ$  were measured using a  $\theta$ - $2\theta$  scan.

The intensity measurements were originally made for a  $C$ -centred, monoclinic cell and the indices were transformed to those of the appropriate hexagonal cell. The existence of the hexagonal cell with rhombohedral symmetry and of the transformation from the monoclinic cell were later confirmed on the diffractometer. Intensity measurements of 633 reflections were made

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over a  $2\theta$  scan range ( $K\alpha_1 - 1.0^\circ$ ) to ( $K\alpha_2 + 1.0^\circ$ ) with a scan rate varying from 3.91 to 29.3° min<sup>-1</sup> depending on the intensity of a preliminary count. Two standard reflections were measured every 48 reflections and these showed no significant deviation in intensity throughout.

Corrections for Lorentz and polarization effects and for absorption for a cylindrical crystal were applied. The latter correction had little effect even though  $\mu = 23.9 \text{ mm}^{-1}$ , because the crystal selected was sufficiently small that  $\mu R = 0.8$ . The maximum and minimum values of  $A^*$  were 3.70 and 3.51 respectively. The structure was initially solved, prior to the absorption corrections, using standard Patterson and Fourier synthesis methods with the program *SHELX* (Sheldrick, 1976). The solution was aided by the fact that for a close-packed structure with a repeat unit of 12 layers only one stacking sequence has rhombohedral symmetry. Final data treatment used the full-matrix least-squares program *CUDLS* and Fourier program *SYMFOU* written internally by J. S. Stephens and J. S. Rutherford respectively. 20 variables were refined including anisotropic temperature factors. Equivalent reflections were averaged to give 245 unique reflections. Of these, 65 were unobserved, *i.e.* had intensities less than  $3\sigma$  where  $\sigma$  is the error based on counting statistics. The final least-squares refinement on  $\sum w(F_o - F_c)^2$  gave  $R_1 = 0.033$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.039$  where  $w = [\sigma^2 + (0.038 \times F^2)]^{-1}$ . Unobserved reflections were given zero weight if  $|F_c| < |F_o|$ . The weighting scheme was chosen to make  $\langle w(|F_o| - |F_c|)^2 \rangle$  independent of  $|F|$ . The secondary-extinction correction, given by Larson (1967), of the form  $F^* = F[1 + 1.5 \times 10^{-7} \times \beta(2\theta)F^2]^{1/2}$  was applied. The average value of shift/error in the final run was 0.009. Atomic scattering factors for neutral Cu and I (Cromer & Waber, 1974) were corrected for anomalous dispersion (Cromer, 1974). The final value of  $[\sum w(|F_c| - |F_o|)^2 / (\text{number}$

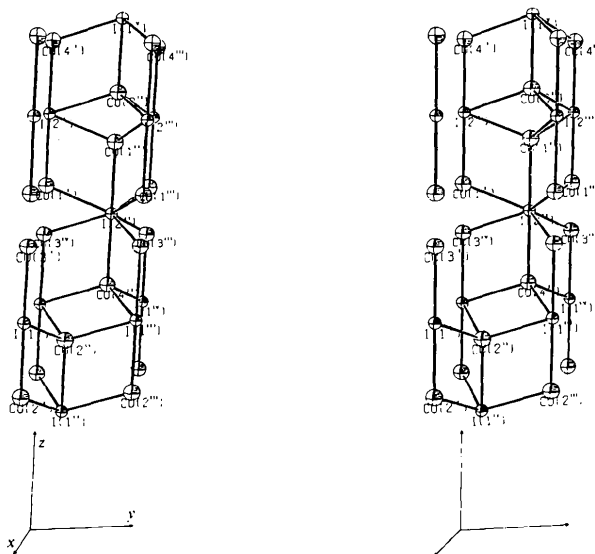


Fig. 1. Stereoscopic view of a segment of the hexagonal unit cell of CuI 12R; vertical length is  $c/3$ . The Cu positions have an occupancy of 0.5.

of reflections - number of variables)<sup>1/2</sup> = 1.5. The final coordinates and  $U_{eq}$  values are given in Table 1.\*

The final difference map showed no positive peaks greater than  $1.49 \text{ e } \text{Å}^{-3}$ , this occurring at  $(0,0,0.0214c)$ . The lowest trough was  $-6.72 \text{ e } \text{Å}^{-3}$ , occurring at  $(0,0,c/2)$ . This is at a position of high symmetry ( $3b$ , point symmetry  $\bar{3}m$ ) and the intensity is about -5% that of an I-atom peak.

Initial data reduction as well as the production of the stereoscopic diagram, Fig. 1, made use of the program *XRAY 76* (Stewart, 1976).

**Discussion.** The structure of CuI 12R may be considered as consisting of close-packed layers of I atoms in planes perpendicular to the  $c$  axis. The structure is closely related to both the cubic close-packed or hexagonal close-packed structures, but with a stacking fault occurring every four layers. The net result is that the sequence repeats every 12 layers and the structure has rhombohedral symmetry. The stacking sequence shown in Fig. 2 can be denoted by the Zhdanov symbol  $(3\ 1)_3$  (Verma & Krishna, 1966 pp. 86-87). The Cu atoms are disordered equally over the tetrahedral holes between the layers of I atoms; thus each Cu-atom site has an occupancy of 0.5. All atoms occur on the special positions, 6(c). Table 2 gives the bond lengths and angles. The entire hexagonal unit cell is shown in Fig. 2. In this diagram bonds are shown to

Table 1. Coordinates and equivalent isotropic temperature factors (hexagonal axis system)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq} (\text{Å}^2)$
I(1)	0	0	0.20824 (2)	0.023 (1)
I(2)	0	0	0.37509 (3)	0.023 (1)
Cu(1)	0	0	0.3129 (1)	0.041 (3)
Cu(2)	0	0	0.1461 (1)	0.042 (3)
Cu(3)	0	0	0.2703 (1)	0.040 (3)
Cu(4)	0	0	0.4375 (1)	0.038 (3)

Equivalent positions

$0, 0, z$	$0, 0, \bar{z}$
$\frac{1}{3}, \frac{2}{3}, \frac{1}{3} + z$	$\frac{1}{3}, \frac{2}{3}, \frac{2}{3} - z$
$\frac{2}{3}, \frac{1}{3}, \frac{1}{3} + z$	$\frac{2}{3}, \frac{1}{3}, \frac{2}{3} - z$

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36222 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

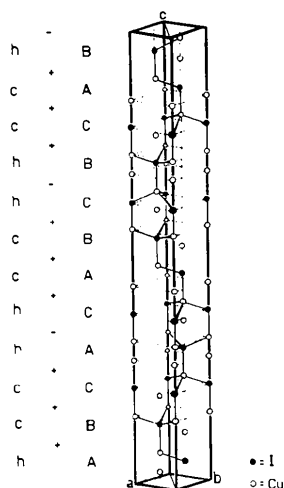


Fig. 2. The hexagonal unit cell of CuI 12R, showing bonds to one half of the equivalent Cu positions. (*h* and *c* denote hexagonal and cubic layers respectively.)

Table 2. Bond distances (Å) and angles (°)

The superscripts refer to the atoms as labelled in Fig. 1.

I(1 <sup>m</sup> )—Cu(2 <sup>n</sup> )	2.615 (2)	I(2 <sup>m</sup> )—Cu(1 <sup>n</sup> )	2.620 (2)
I(1 <sup>l</sup> )—Cu(4 <sup>n</sup> )	2.615 (2)	I(2 <sup>m</sup> )—Cu(3 <sup>n</sup> )	2.620 (2)
I(1 <sup>m</sup> )—Cu(2 <sup>m</sup> )	2.607 (6)	I(2 <sup>m</sup> )—Cu(1 <sup>m</sup> )	2.610 (6)
I(1 <sup>l</sup> )—Cu(3 <sup>m</sup> )	2.604 (6)	I(2 <sup>m</sup> )—Cu(4 <sup>m</sup> )	2.619 (5)
Cu(2 <sup>n</sup> )—I(1 <sup>m</sup> )—Cu(2 <sup>m</sup> )	109.23 (8)	Cu(1 <sup>n</sup> )—I(2 <sup>m</sup> )—Cu(1 <sup>m</sup> )	109.01 (9)
Cu(2 <sup>m</sup> )—I(1 <sup>m</sup> )—Cu(4 <sup>n</sup> )	109.64 (11)	Cu(1 <sup>n</sup> )—I(2 <sup>m</sup> )—Cu(4 <sup>m</sup> )	109.94 (12)
Cu(2 <sup>m</sup> )—I(1 <sup>l</sup> )—Cu(3 <sup>n</sup> )	109.70 (12)	Cu(1 <sup>n</sup> )—I(2 <sup>m</sup> )—Cu(3 <sup>n</sup> )	109.94 (12)
Cu(4 <sup>n</sup> )—I(1 <sup>l</sup> )—Cu(4 <sup>m</sup> )	109.31 (8)	Cu(3 <sup>m</sup> )—I(2 <sup>m</sup> )—Cu(3 <sup>n</sup> )	109.00 (9)
I(1 <sup>l</sup> )—Cu(2 <sup>m</sup> )—I(1 <sup>m</sup> )	109.24 (12)	I(2 <sup>m</sup> )—Cu(1 <sup>n</sup> )—I(2 <sup>m</sup> )	109.00 (12)
I(1 <sup>l</sup> )—Cu(2 <sup>m</sup> )—I(1 <sup>m</sup> )	109.69 (12)	I(2 <sup>m</sup> )—Cu(1 <sup>n</sup> )—I(2 <sup>m</sup> )	109.95 (12)
I(2 <sup>m</sup> )—Cu(3 <sup>n</sup> )—I(2 <sup>m</sup> )	109.00 (12)	I(1 <sup>m</sup> )—Cu(4 <sup>m</sup> )—I(1 <sup>m</sup> )	109.31 (11)
I(2 <sup>m</sup> )—Cu(3 <sup>n</sup> )—I(1 <sup>l</sup> )	109.94 (12)	I(1 <sup>m</sup> )—Cu(4 <sup>m</sup> )—I(2 <sup>m</sup> )	109.63 (11)

one-half of the positions over which the Cu atoms are disordered, thus indicating the most reasonable ordering of the atoms in a given domain of the crystal. The other set of positions for the disordered Cu atoms are shown but without bonds.

The *a* cell dimension of polytype 12R is 4.265 (2) Å. This may be compared to the same dimension in polytype 6H (Kurdyumova & Baranova, 1961), *a* = 4.25 (1) Å, and the corresponding distance in  $\gamma$ -CuI(cubic) (Miyake, Hoshino & Takenaka, 1952)  $a_c/\sqrt{2} = 4.280$  Å. The average spacing between layers of I atoms, given by  $\langle S \rangle = c/n$  (where *n* = number of layers, formula units, in the hexagonal unit cell), is comparable with the corresponding values in polytype 6H and in  $\gamma$ -CuI. They are: CuI 12R:  $\langle S \rangle = 41.96$  (1) Å/12 = 3.497 (1) Å; CuI 6H:  $\langle S \rangle = 20.86$  (6) Å/6 = 3.48 (1);  $\gamma$ -CuI(cubic):  $S = 6.052$  Å/ $\sqrt{3} = 3.494$ .

The ratio of the layer spacing *S* to the unit-cell dimension *a* is a measure of how closely the structure simulates close packing. The ideal value of *S/a* is 0.8165. For polytype 12R  $\langle S \rangle/a = 0.8199$  indicating

elongation along the *c* axis. The separations *S* between successive layers of I atoms are 3.503 (2) Å for adjacent layers of I(2), 3.497 (2) Å for adjacent layers I(1) to I(2), and 3.489 (2) Å for adjacent layers of I(1). The latter spacing is slightly but significantly different from the other two.

The sum of the atomic radius of Cu and the covalent radius of I is 1.28 + 1.33 = 2.61 Å whereas the sum of the ionic radii is 0.98 + 2.12 = 3.10 Å. The actual bond lengths in CuI are identical to the sum of the covalent radii. Thus the bonding in CuI might be described as homopolar as was also noted for ZnS (Verma & Krishna, 1966, pp. 74–77).

The phenomenon of polytypism may be an important consideration in the interpretation of powder diffraction data of the different phases of CuI at various temperatures as there are apparently only small energy differences between different polytypes. It has been suggested that for ZnS, which presently is known to have 131 polytypes (Rai, 1972), transformation from 3C (sphalerite) to 2H (wurtzite) occurs *via* intermediate polytypes (Rai, Srivastava & Krishna, 1970). A phase diagram of CuI (Mao-Chia Yang & Schwartz, 1968) indicates that at elevated pressures CuI has at least three more phases other than the already established  $\alpha$ ,  $\beta$  and  $\gamma$  phases. These authors suggested that different phases of CuI may be polytypic in nature. The crystals of CuI 12R cleave readily perpendicular to [001] and are easily crumbled. An X-ray powder photograph of ground crystals of polytype 12R reveals that, upon grinding, the material reverts back to  $\gamma$ -CuI which is the normal phase of CuI at room temperature. Weissenberg photographs of several individual crystals from the batch all showed the pattern for polytype 12R. It is interesting to note that polytype 6H (Kurdyumova & Baranova, 1961) also reverts back to  $\gamma$ -CuI, upon annealing at 373 K.

Electron diffraction data from thin films of polytype 6H obtained by Kurdyumova & Baranova (1961) have been interpreted by them in terms of a model structure which contained double layers of Cu atoms in the tetrahedral holes alternately every two layers of I atoms (*i.e.*...I Cu Cu I I Cu Cu I...). More recently Bührer & Hälgl (1977) in their treatment of powder neutron diffraction data for  $\gamma$ -CuI obtained an improvement in their refinement by employing the method of Helmholtz (1935) in which the Cu atoms are statistically distributed on metastable positions which are located on the tetrahedral diagonals of the occupied hole. The same authors found that for the  $\beta$  phase of CuI their diffraction data could best be interpreted with Cu atoms statistically distributed into both tetrahedral and octahedral sites. These authors suggest that ionic conductivity in the  $\gamma$ -phase at elevated temperatures may occur through tunnelling of Cu ions through the faces of the tetrahedral sites, while for  $\beta$ -CuI the octahedral sites form channels, parallel to the *c* axis,

along which the Cu ions can move. The temperature factors for the Cu atoms in octahedral sites were appropriately large.

In our single-crystal X-ray study of CuI 12R no electron density is found in octahedral sites. The possibility of the crystal containing domains with the layered kind of structure proposed by Kurdyumova & Baranova (1961) is considered unlikely and we prefer the local ordering indicated in Fig. 2, where each I atom is surrounded by a tetrahedron of Cu atoms, or perhaps a completely random distribution over the tetrahedral sites. The temperature factors for Cu are somewhat larger than those for I (see Table 1). The thermal motion is essentially isotropic. Unfortunately the conductivity of polytype 12R could not be determined because the crystals obtained were too small.

Clearly techniques for obtaining good single crystals of CuI in its various phases and polytypes are desirable in order to clarify the role of structure in determining ionic conductivity. The use of PH<sub>3</sub>-saturated solvents may prove useful in the synthesis of single crystals of metal iodides.

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## Structure of Magnesium Isothiocyanate Tetrahydrate

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**Abstract.** Mg(NCS)<sub>2</sub>·4H<sub>2</sub>O, monoclinic,  $P2_1/a$ ,  $a = 7.488$  (2),  $b = 9.030$  (2),  $c = 7.869$  (2) Å,  $\beta = 113.63$  (1)°,  $V = 487.5$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.45$  Mg m<sup>-3</sup>. The structure has been determined by Patterson and Fourier methods and has been refined to  $R = 0.029$  for 807 observed reflections. The structure consists of Mg(NCS)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> molecules which are interconnected by three kinds of O—H···S and one kind of O—H···O hydrogen bonds. Mg has a centrosymmetric octahedral coordination with Mg—N 2.102 (2), Mg—O 2.047 (2) and 2.126 (2) Å.

0567-7408/82/041263-03\$01.00

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**Introduction.** This study was stimulated by our interest in hydrogen bonds between water molecules and sulphur (Mereiter, Preisinger, Baumgartner, Heger, Mikenda & Steidl, 1982). Colourless platy crystals of the title compound were obtained by mixing two equimolar aqueous solutions of MgSO<sub>4</sub>·7H<sub>2</sub>O and Ba(SCN)<sub>2</sub>·3H<sub>2</sub>O, filtering off the precipitated BaSO<sub>4</sub>, and evaporating the solution obtained at room temperature.

Intensity data for a crystal 0.3 × 0.2 × 0.1 mm were collected on a Philips PW 1100 four-circle

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