Determination of the structure of β-CuI by high-resolution neutron powder diffraction

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Abstract. The structure of the beta form of copper(I) iodide has been investigated. The hexagonal β-CuI exists as a single phase between 647 K and 655 K and shows marked anisotropy in its thermal expansion within this small temperature range. The high quality of the diffraction data has allowed the corrected structure for β-CuI to be determined in space group $P\bar{3}m1$, with I in 2(d) sites at $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, \bar{z})$ with $z = 0.242(1)$, thus forming a slightly distorted hexagonal close-packed array. The Cu^+ are situated in the tetrahedral voids, predominantly on 2(d) sites at $z = 0.6214(8)$ but with a significant fraction of the cations disordered onto 2(d) sites with $z = 0.8786(8)$. The relationship between this and other previously published structures of β-CuI is discussed.

1. Introduction

There have been extensive studies of copper(I) iodide at elevated temperatures, largely because it displays fast-ion conduction, with the α-form having one of the highest ionic conductivities for a compound with a face-centred cubic (FCC) anion substance. At ambient pressure CuI exists in three stable phases below its melting point $T_m = 878$ K. At room temperature CuI has the cubic zincblende structure (γ-CuI, $F\bar{4}3m$) and at $T \sim 642$ K it transforms to the β-phase. The structural transition results in a change from an FCC close-packed I^- sublattice to a slightly distorted hexagonal close-packed (HCP) one. However, the locations of the Cu^+ cations within β-CuI have not been satisfactorily resolved. During the $\beta \rightarrow \alpha$ transition at $T \sim 680$ K the anion sublattice reverts to FCC packing with the cations statistically distributed all over the tetrahedral interstices in space group $Fm\bar{3}m$. On increasing temperature in both γ- and α-phases the cations exhibit increasingly large anharmonicity in their thermal vibrations [1].

The specific heat capacity of CuI, C_p, starts to increase anomalously around 200 K below the $\gamma \rightarrow \beta$ transition and decreases in the α phase [2]. This behaviour suggests a second-order (order$\rightarrow$disorder) $\gamma \rightarrow \alpha$ transformation, interrupted by the two strongly first-order $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions. Molecular dynamics simulations have failed to stabilize the hexagonal β-phase, and instead observe a continuous transition from $\gamma \rightarrow \alpha$ with increasing temperature [3]. Consideration of the p–T phase diagram of CuI [4] shows that at pressures greater than ~ 2 kbar the $\gamma \rightarrow \alpha$ transformation takes place via a different phase (labelled CuI-IV in [4]), which has recently been shown to possess a rhombohedral structure with a slightly distorted cubic close-packed I^- sublattice [5], in common with γ- and α-CuI. Therefore, at relatively modest pressures the temperature evolution of the fast-ion behaviour can be considered as an increasing cation disorder within an essentially

rigid anion sublattice. The above discussion serves to highlight the anomalous nature of the β-phase and motivates a detailed investigation of its structure.

Earlier diffraction measurements have often failed to isolate the β-phase without contamination from the neighbouring phases [6] and previous determinations of the structure of β-CuI have been inconclusive, proposing a number of related hexagonal structures. The earliest x-ray diffraction measurements [2, 7] determined the structure of β-CuI to be wurtzite ($P6_3mc$), in common with the high-temperature phases β-CuCl and β-CuBr. However, a subsequent neutron diffraction [1] study clearly showed the 001 reflection in β-CuI, which is absent in $P6_3mc$ symmetry. These authors proposed an alternative model, retaining the HCP I$^-$ sublattice but redistributing the Cu$^+$ over the tetrahedral holes using space group $P\bar{6}m2$. Evidence for cation disorder was also observed, with $\sim 30\%$ Cu$^+$ located in octahedral interstices, though the general agreement between observed and calculated intensities was significantly poorer than that obtained for the neighbouring cubic γ- and α-phases. Furthermore, this structure contains anomalously short Cu$^+$–Cu$^+$ distances ($c/4 \simeq 1.8$ Å) leading Sakuma [8] to propose a different structure in space group $p3m1$. This also has an HCP I$^-$ sublattice but now all four ions ($2\times$Cu$^+$ and $2\times$I$^-$) are in symmetry-independent sites, leading to two distinct and rather distorted tetrahedral Cu$^+$ environments.

This paper describes a high-resolution powder neutron diffraction experiment which re-examines the β-CuI phase. Using good quality, single-phase data, it has been possible to determine its correct time-averaged structure.

2. Experimental method

Commercially available CuI powder supplied by the Aldrich Chemical Company, of purity 99.999%, was used in these experiments. After grinding, 4.2 cm^3 of material was sealed under vacuum inside a silica ampoule. The diffraction measurements were performed on the high-resolution powder diffractometer (HRPD) [9] at the ISIS facility, UK, using a furnace designed for neutron scattering experiments. Diffraction data were collected in the backscattering detector bank ($168° < 2\theta < 176°$) over a d-spacing range 0.8 Å $< d < 3.8$ Å with a resolution $\Delta d/d \sim 8 \times 10^{-4}$. Although the structures adopted by CuI on increasing temperature are relatively simple the high instrumental resolution is required in those temperature ranges where two neighbouring phases co-exist. Measurements were taken every 4 K across the β-phase, with data collection starting ~ 10 min after reaching the required temperature, and typical counting times of ~ 90 min at each temperature.

In order to take account of the scattering and absorption from the silica ampoule, a polynominal function was fitted to the background regions of a diffraction pattern collected at ambient temperature, excluding the regions containing γ-CuI Bragg peaks. This polynomial function was subsequently used to extrapolate the background over the regions of the Bragg peaks and this calculated background was subtracted from the data collected at higher temperatures. Any small increases in the measured background at higher temperatures could be attributed to an increase in coherent diffuse scattering from CuI, and the background polynominal was further refined to account for this. Rietveld profile refinements of the corrected diffraction data were performed using the program TF12LS and its multiphase derivative [10], which are based upon the Cambridge Crystallographic Subroutine Library [11].

The quality of the fit to the experimental diffraction data was assessed using the usual χ^2 statistic defined as $\chi^2 = R_{wp}^2/R_{exp}^2$ where the weighted profile R-factor, R_{wp}, is

$$R_{\text{wp}}^2 = \sum_{i=1}^{N_p} \frac{(y_{i\text{obs}} - y_{i\text{calc}})^2}{(\sigma y_{i\text{obs}})^2} \bigg/ \sum_{i=1}^{N_p} \frac{(y_{i\text{obs}})^2}{(\sigma y_{i\text{obs}})^2}$$

and the expected R-factor, R_{exp}, is

$$R_{\text{exp}}^2 = (N_p + C - P) \bigg/ \sum_{i=1}^{N_p} \frac{(y_{i\text{obs}})^2}{(\sigma y_{i\text{obs}})^2}.$$

N_p is the number of data points, P is the number of fitted parameters and C is the number of parameter constraints. $y_{i\text{obs}}$ and $y_{i\text{calc}}$ are the observed and calculated intensities, respectively and $\sigma y_{i\text{obs}}$ is the estimated standard deviation on $y_{i\text{obs}}$.

3. Results

On increasing temperature, diffraction lines from the β-CuI phase were first observed at 643 K and all the remaining γ-CuI lines had disappeared at the next temperature, 647 K. The first evidence of the cubic α-CuI diffraction pattern appeared at 659 K, with all β-CuI having transformed at 667 K. Attempts to determine the structure of the β-phase were made using the data collected at 655 K. As expected, this could be successfully indexed on a hexagonal unit cell containing two CuI formula units. A structurally independent fit to the data using unconstrained peak intensities (and also varying the unit cell and background parameters) gave an excellent agreement between observed and calculated profiles ($\chi^2 = 1.08$, $R_{\text{wp}} = 3.52\%$ and $R_{\text{exp}} = 3.39\%$). The refined cell parameters were $a = 4.304\,19(2)$ Å and $c = 7.185\,10(5)$ Å. Analysis of the fitted profile showed no evidence for additional reflections not consistent with the hexagonal unit cell and the intensities of the individual reflections indicated no systematic absences. The 001 reflection was clearly visible when the instrument choppers were re-phased to measure the appropriate d-spacing range.

Attempts to determine the correct structure of β-CuI were made with the assumption that the I^- sublattice approximates to hexagonal close packing. There is necessarily a small distortion owing to the difference between the observed c/a ratio of 1.6693 and the ideal value of 1.6330. I^- were therefore placed at $(0, 0, 0)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$. The presence of Cu^+ in tetrahedral environments within the neighbouring γ- and α-phases suggests that these sites be used initially for determining starting models for the structure of β-CuI. The tetrahedral interstices are located at $(0, 0, \frac{3}{8})$, $(\frac{1}{3}, \frac{2}{3}, \frac{7}{8})$, $(0, 0, \frac{5}{8})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{8})$, corresponding to positions A, B, C and D in figure 1. There are three different ways in which the two cations can be distributed over the four available sites. Attempts to fit the data to each of these models have been made, using the requirement of physically reasonable parameters and the goodness-of-fit factor χ^2, defined in section 2, to choose between them.

3.1. Model 1

With suitable shift of the origin the first model listed in figure 1 corresponds to space group $P\bar{6}_3mc$ with I^- and Cu^+ in 2(b) sites at $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, z + \frac{1}{2})$. The iodine positional parameter must have $z_I = 0$ to fix the origin, whilst $z_{Cu} \sim \frac{3}{8}$. This structure is formally equivalent to wurtzite as proposed previously [2, 7]. As expected, this model gives a relatively poor fit to the data with $\chi^2 = 2.35$. It was not possible to obtain a stable refinement with z_{Cu} varied or by introducing disorder onto the Cu^+ sublattice.
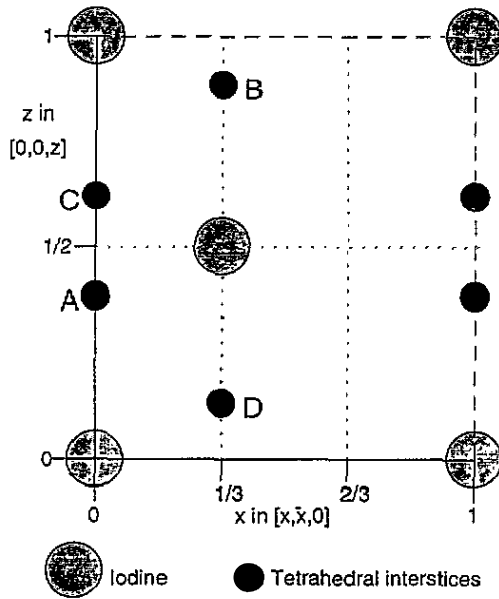
Model	Cu$^+$ sites	Space group	Comments
1	A and B	$P6_3mc$	Wurtzite structure [2,7]
2	A and C	$P\bar{6}m2$	Ordered version of [1]
3	B and C	$P\bar{3}m1$	[8] plus centre of symmetry

Figure 1. The possible ordered structures of β-CuI, derived by distributing the two Cu$^+$ over the four available tetrahedral interstices within the HCP I$^-$ sublattice.

3.2. Model 2

The second alternative belongs to space group $P\bar{6}m2$ with two symmetry-independent iodine ions, I1 in 1(a) at $(0, 0, 0)$ and I2 in 1(d) at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$. The Cu$^+$ are located in a twofold set in 2(g) at $(0, 0, z)$ and $(0, 0, \bar{z})$ with $z_{Cu} \sim \frac{3}{8}$. The structure represents the fully ordered limit of the model of Bührer and Hälg [1]. Refinements of the diffraction data gave a poor fit using the ordered model, with $\chi^2 \sim 2.78$. The quality of the fit improved on introducing disorder on the cation sublattice, the lowest value of $\chi^2 = 1.65$ obtained with $\sim 18\%$ of Cu$^+$ on the octahedral sites, rather than the remaining tetrahedral ones, close to the structure reported previously [1].

3.3. Model 3

The final model to be considered places both ionic species in the 2(d) positions of space group $P\bar{3}m1$ at $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, \bar{z})$ with $z_1 \sim \frac{1}{4}$ and $z_{Cu} \sim \frac{5}{8}$. Refinements using this model led to a fit marginally better than the disordered $P\bar{6}m2$ case, with $\chi^2 = 1.56$. However, significant differences between the observed and calculated intensities of the reflections remained. Attempts to improve the quality of the fit by removing the centre of symmetry (space group $P3m1$, as suggested by Sakuma [8]) failed to converge owing to excessive correlations between the z positional parameters.

    As an alternative, the possibility of disorder within the centro-symmetric structure ($P\bar{3}m1$) was considered, with partial occupancy of the original 2(d) sites and the remaining
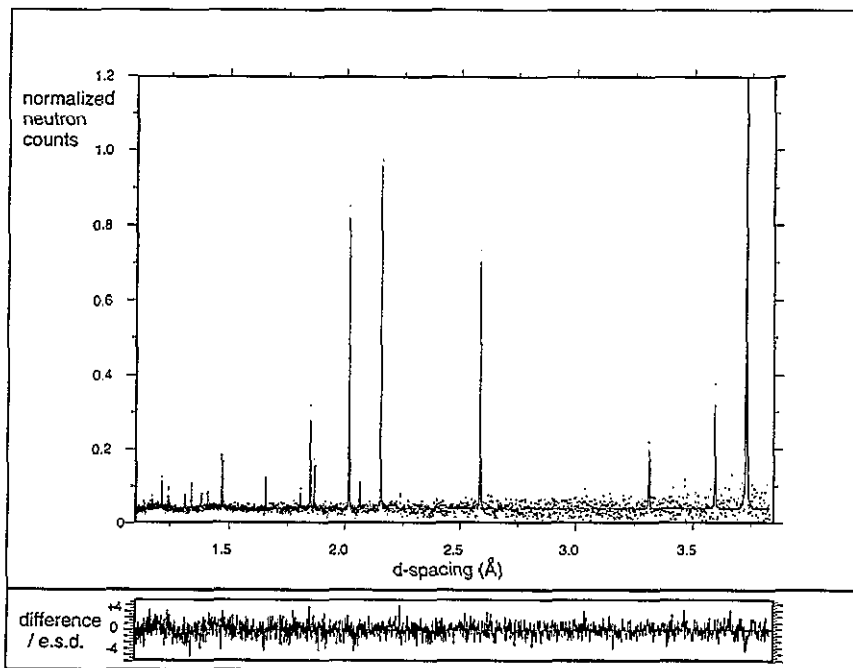
Figure 2. Time-of-flight Rietveld refinement of the diffraction data from β-CuI at 655 K. The dots are the experimental points and the line is a least-squares fit to the data using the parameters listed in table 1. The quality of the fit illustrated in the lower trace, which plots the difference (measured−calculated) divided by the estimated standard deviation on each data point.

cations, labelled Cu2, located in 2(d) sites in the alternative tetrahedral interstices at $z_{Cu2} \sim \frac{7}{8}$. This model gave an excellent fit to the data (see figure 2) with $\chi^2 = 1.10$ and approximately 15% of the cations on the Cu2 sites. Refinements using anisotropic or anharmonic thermal vibrations of the cations, as observed in the neighbouring γ- and α-phases, gave no improvement in the quality of the fit to the experimental data. Likewise, attempts to model the diffraction data by allowing a fraction of the cations to occupy octahedral sites produced no significant decrease in χ^2.

4. Discussion

Table 1 summarizes the results of the structural refinement of the diffraction data collected from the β-phase of CuI at 655 K, using the $P\bar{3}m1$ structure described in the previous section. In this structure, shown schematically in figure 3, the I^- sublattice is only slightly distorted from HCP. Each I^- has six like neighbours at a distance of 4.30(1) Å, plus three at 4.27(1) Å and three at 4.77(1) Å. The two alternative sets of tetrahedral cation sites, Cu1 and Cu2, form layers of edge-sharing CuI_4 tetrahedra perpendicular to the c-axis. The tetrahedra are slightly distorted, such that each Cu1 has three I^- at a distance 2.68(1) Å and a fourth at 2.71(1) Å, and each Cu2 has three I^- at 2.60(7) Å and a fourth at 2.72(7) Å. The two tetrahedral sites are a distance 1.76(8) Å apart along the c-axis, separated by a common tetrahedral face (sites A and C in figure 1). As discussed previously [8], this distance is comparable with twice the tabulated Cu^+ ionic radius. It is, therefore, unlikely
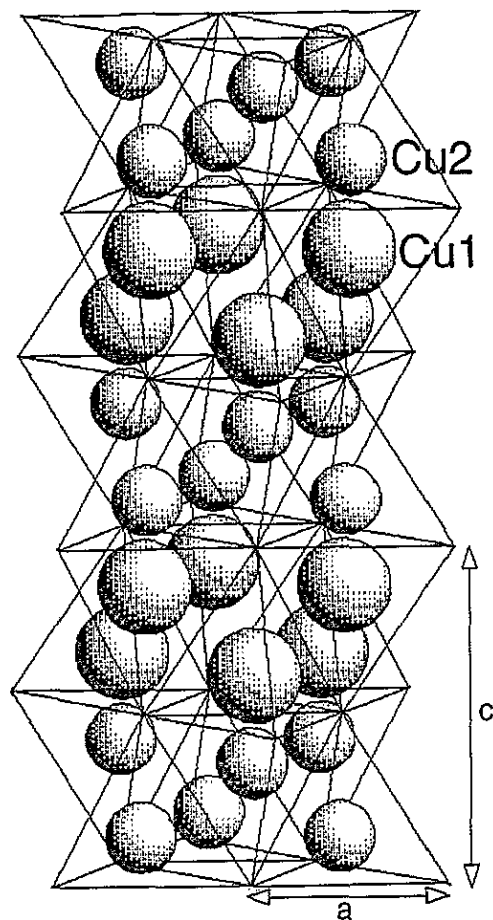
Figure 3. Schematic diagram of the structure of β-CuI. The anions are at the vertices of the solid line tetrahedra in a slightly distorted HCP arrangement. With increasing temperature an increasing proportion of cations leaves the regular tetrahedral sites (Cu1) and occupies the alternate set of tetrahedral voids (Cu2).

that these two sites will be simultaneously occupied but rather that this models the preferred direction of Cu^+ disorder in this phase.

The temperature variation of the unit-cell dimensions, illustrated in figure 4, shows significantly anisotropic behaviour. A consequence of the decrease in the c-axis with increasing temperature is that the c/a ratio falls, approaching the 'ideal' value of 1.6330, characteristic of hexagonal close packing. The latter would also require that the anion positional parameter has the value $z_1 = \frac{1}{4}$, though the relatively larger errors on the positional parameters do not provide any evidence for significant changes with temperature. The isotropic thermal vibration parameter B_1 for the anion shows little change with temperature whilst that for Cu^+ increases from 10.6(5) at 643 K to 12.6(5) at 667 K. The other principal change with temperature is the increased cation occupation of the Cu2 sites. As illustrated in figure 5, over the $\sim$ 20 K temperature range over which the β-CuI phase exists, the extent of cation disorder (defined as the proportion of Cu^+ that leaves the Cu1 sites to occupy Cu2 sites) increases from 10.3(13)% to 22.2(9)%. In terms of the development of
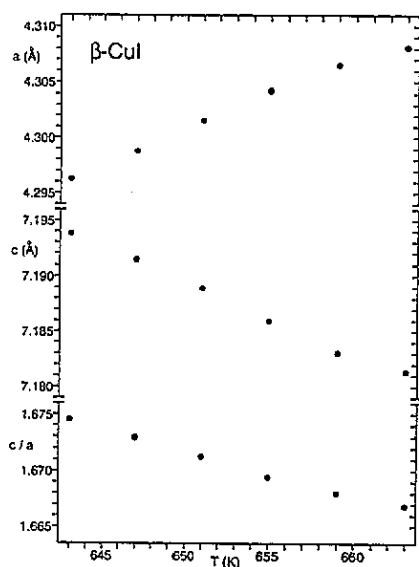
Figure 4. The temperature variation of the unit-cell constants and the hexagonal c/a ratio of β-CuI. The errors on the experimental data are smaller than the size of the points.
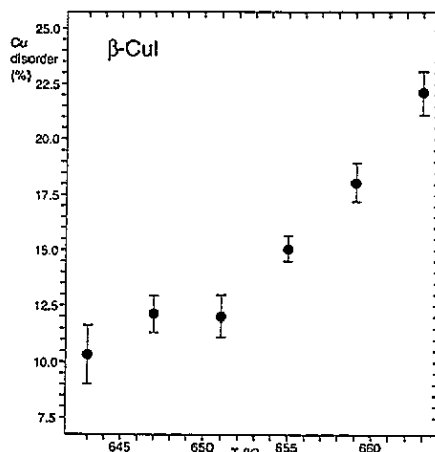

Figure 5. The temperature variation of the fraction of Cu$^+$ that leaves the regular lattice sites (Cu1) and occupies the alternate set of tetrahedral sites (Cu2) in β-CuI.

Table 1. Summary of the structural parameters of β-CuI determined by Rietveld definement of the powder neutron diffraction data collected at 655 K.

Space group	$P\bar{3}m1$
Unit cell dimensions	$a = 4.304\,19(2)$ Å $c = 7.185\,10(5)$ Å $c/a = 1.6693$
Atom positions	I in 2(d) at $(\frac{1}{3}, \frac{2}{3}, z_I)$ and $(\frac{2}{3}, \frac{1}{3}, \bar{z}_I)$ Cu1 in 2(d) at $(\frac{1}{3}, \frac{2}{3}, z_{Cu1})$ and $(\frac{2}{3}, \frac{1}{3}, \bar{z}_{Cu1})$ Cu2 in 2(d) at $(\frac{1}{3}, \frac{2}{3}, z_{Cu2})$ and $(\frac{2}{3}, \frac{1}{3}, \bar{z}_{Cu2})$
Refined parameters	Isotropic thermal parameters B_I, B_{Cu1} and B_{Cu2} Cu positional parameters z_I, z_{Cu1} and z_{Cu2} Cu fractional site occupancies n_{Cu1} and n_{Cu2}
Parameter constraints	$B_{Cu2} = B_{Cu1}$ $n_{Cu2} = 1 - n_{Cu1}$
Parameter values	$B_I = 5.2(2)$ Å^2 $B_{Cu1} = 12.9(3)$ Å^2 $z_I = 0.242(1)$ $z_{Cu1} = 0.6214(8)$ $z_{Cu2} = 0.8786(8)$ $n_{Cu1} = 0.851(7)$

the thermally induced cation disorder, β-CuI therefore acts as an intermediate between the γ- and α-phases. In the former, the cations remain predominantly on their regular sites but undergo large, anharmonic thermal vibrations. In the latter, the cations are completely disordered, with on average 50% residing in the alternate set of tetrahedral voids in the FCC anion sublattice.

5. Conclusions

The crystal structure of the β-phase of copper(I) iodide has been investigated using high-resolution neutron powder diffraction in the temperature range 643 K to 663 K. The hexagonal unit cell has $a = 4.304\ 19(2)$ Å, $c = 7.185\ 10(5)$ Å at $T = 655$ K. The diffraction data have been used to critically assess different models for the structure of β-CuI, including those proposed in the literature. The structure that best fits the experimental data is in space group $P\bar{3}m1$, with I^- in 2(d) sites at $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, \bar{z})$ with $z = 0.241(1)$, thus forming a slightly distorted HCP array. The Cu^+ are situated in the tetrahedral voids, predominantly on 2(d) sites at $z = 0.618(1)$ but with 15.0(6)% of the cations disordered onto 2(d) sites with $z = 0.863(9)$.

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