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# The high-temperature structural behaviour of copper(I) iodide

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**Abstract.** The structural behaviour of copper(I) iodide, CuI, has been investigated between room temperature and its melting point ( $T_M = 878$  K) using neutron powder diffraction. Detailed measurements have been made in the vicinity of the two known structural phase transitions  $\gamma \rightarrow \beta$  and  $\beta \rightarrow \alpha$ , which are observed at  $643 \pm 2$  K and  $673 \pm 8$  K. Within the zinc-blende-structured  $\gamma$ -phase (space group  $F\bar{4}3m$ ) increasing disorder of the  $\text{Cu}^+$  ion sublattice is observed as temperature approaches the  $\gamma \rightarrow \beta$  transition, in addition to a non-linear thermal expansion. The hexagonal  $\beta$ -phase (space group  $P\bar{3}m1$ ) is observed as a single phase in the temperature range 645–668 K, but on first heating it is found to coexist with a rhombohedral phase. This transient phase was observed in isolation for only a short time but this was sufficient to show that its structure was that of CuI-IV (space group  $R\bar{3}m$ ), which had only been observed previously at elevated pressures. The high-temperature phase  $\alpha$ -CuI has  $Fm\bar{3}m$  symmetry with  $\text{Cu}^+$  ions distributed randomly over all the tetrahedral sites within the cubic close-packed  $\text{I}^-$  sublattice.

## 1. Introduction

At ambient pressure CuI is thought to exist in three stable phases between room temperature and its melting point  $T_M = 878$  K. At  $\sim 300$  K CuI has the cubic zinc blende structure ( $\gamma$ -CuI) and at  $T \sim 643$  K it transforms to the  $\beta$ -phase. The structural transition results in a change from a face-centred cubic (FCC) close packed  $\text{I}^-$  sublattice to a slightly distorted hexagonal close-packed (HCP) one, the structure of which has been described in Keen and Hull [1]. During the  $\beta \rightarrow \alpha$  transition at  $T \sim 673$  K the anion sublattice reverts to FCC with the cations statistically distributed over all the tetrahedral interstices and displaying large anharmonic thermal vibrations.

There have been many structural studies of the cuprous halides, largely because at elevated temperatures some of the phases display fast-ionic conduction. Indeed, CuI has one of the highest ionic conductivities for a compound with an FCC anion lattice. The conductivity  $\sigma$  approaches  $0.1 \Omega^{-1} \text{cm}^{-1}$  in the  $\gamma$ -phase, is slightly higher in the  $\beta$ -phase and in the  $\alpha$ -phase it reaches  $\sigma \sim 1 \Omega^{-1} \text{cm}^{-1}$  [2, 3]. Most structural studies have therefore attempted to determine the nature of the ionic disorder which facilitates this ionic motion, and thus deduce the mechanism for conduction. In the FCC phases of cuprous halides it is generally accepted that the mobile  $\text{Cu}^+$  ion undergoes anharmonic thermal motion at even modest temperatures, and that this results in anomalous  $\text{Cu}^+$  ion displacements in  $\langle 111 \rangle$  directions towards the face centres of the surrounding  $\text{I}^-$  tetrahedron cage. Previous work has attempted to deduce the most physical description of this motion, although a simple split site model, where (in  $\gamma$ -CuI)  $\text{Cu}^+$  ions are disordered from 4(c) sites at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  etc into 16(e) sites at  $(x, x, x)$  etc with  $x \sim 0.29$  [e.g. 4, 5] provides as good a fit to the available

diffraction data as the more sophisticated anharmonic potential models [e.g. 6, 7]. This implies that the  $\text{Cu}^+$  ions move from tetrahedral to tetrahedral sites via octahedral 4(b) sites at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  etc in (111) directions, a mechanism proposed by Azaroff [8].

In this present study, neutron powder diffraction measurements have been made at several temperatures spanning the whole temperature range between room temperature and the melting point in order to investigate the thermally induced disorder in CuI. Particular attention has been paid to the region around the two phase transitions, and to the existence of another phase which has been observed at these temperatures and ambient pressure for the first time.

## 2. Experimental method

CuI powder from the Aldrich Chemical company, of stated purity 99.999%, was used in these experiments. After grinding, 2.5 cm<sup>3</sup> of material was sealed under vacuum inside a thin-walled silica ampoule. The diffraction measurements were performed on the Polaris powder diffractometer [9] at the ISIS facility, UK, using a furnace designed for neutron scattering experiments. Diffraction data were collected in all available detector banks over a  $d$ -spacing range  $0.5 < d(\text{\AA}) < 12.0$ , although refinements reported here were carried out using the highest-resolution backscattering detectors ( $135^\circ < 2\theta < 160^\circ$ ) with a resolution  $\Delta d/d \sim 5 \times 10^{-3}$ . A series of short ( $\sim 5$  min) runs were carried out at each temperature, exploiting the ability of time of flight neutron powder diffraction to measure the whole powder pattern simultaneously. Data of good enough quality for multiphase profile refinement were obtained by adding together 10 such runs. Short runs were particularly necessary to assess the transient nature of the rhombohedral phase. Two different samples were heated, each showing the same behaviour, with the same transition temperatures and lattice expansions. The first sample therefore could be used to pinpoint the most pertinent temperature regime for the measurements using the second sample. The results described here are from runs at 23 temperatures of the second sample and from one run made on the high-resolution powder diffractometer (HRPD) [10] during the measurements which yielded the work described in Keen and Hull [1] and to which readers are referred to for an experimental description. The data correction procedure, taking account of absorption and silica background, was identical to that described in [1]. Rietveld profile refinements of the normalized diffraction data were performed using the program TF12LS and its multiphase derivative [11], which are based upon the Cambridge crystallographic subroutine library [12]. The usual  $\chi^2$  statistic was used to assess the relative merits of different structural models applied to the data (where  $\chi$  is the ratio of the standard weighted profile  $R$  factor,  $R_w$ , and the expected  $R$  factor,  $R_{\text{exp}}$ ).

## 3. Results

A qualitative overview of the behaviour of the neutron powder diffraction patterns from CuI with increasing temperature is shown in figure 1. There is a large decrease in peak height as temperature is raised, and two clear phase transitions. The highest temperature phase has only very weak intensities which is indicative of a high degree of structural disorder. Closer inspection shows that some peaks within the  $\beta$ -phase temperature regime ( $643 \text{ K} < T < 673 \text{ K}$ ) are only visible at the lower temperatures. This is evidence of the presence of another phase (see section 3.4 below).

Table 1. Structural parameters of  $\gamma$ -CuI in the temperature range 303–643 K.  $\gamma$ -CuI; Space group:  $F\bar{4}3m$ ; Atom positions: I in 4(a) at (0, 0, 0) etc, CuI in 16(e) at ( $x_{\text{CuI}}, x_{\text{CuI}}, x_{\text{CuI}}$ ) etc, Cu2 in 16(e) at ( $x_{\text{Cu2}}, x_{\text{Cu2}}, x_{\text{Cu2}}$ ) etc; Refined parameters: Isotropic thermal parameters  $B_{\text{I}}$ ,  $B_{\text{Cu1}}$  and  $B_{\text{Cu2}}$ , Cu positional parameters  $x_{\text{Cu1}}$  and  $x_{\text{Cu2}}$ , Cu site occupancies  $n_{\text{Cu1}}$  and  $n_{\text{Cu2}}$ ; Parameter constraints:  $B_{\text{Cu2}} = B_{\text{Cu1}}$ ,  $n_{\text{Cu2}} = 1 - n_{\text{Cu1}}$  and  $x_{\text{Cu1}} = -x_{\text{Cu2}}$ .

$T$ (K)	No runs	$\chi^2$	$V_{\text{fraction}}$	$a$ (Å)	$V/Z$ (Å <sup>3</sup> )	$B_{\text{I}}$ (Å <sup>2</sup> )	$B_{\text{CuI}}$ (Å <sup>2</sup> )	$x_{\text{CuI}}$	$n_{\text{CuI}}$
303	1–5	1.18	1.00	6.052 14(8)	55.42	1.3(1)	1.4(1)	0.265(2)	0.250(1)
373	1–5	1.41	1.00	6.056 45(6)	55.54	1.5(1)	1.6(2)	0.267(2)	0.2492(9)
473	1–5	1.34	1.00	6.066 45(7)	55.81	1.8(1)	1.8(2)	0.271(1)	0.248(1)
573	1–5	1.30	1.00	6.084 74(9)	56.32	2.4(1)	2.8(3)	0.276(1)	0.250(1)
623	1–5	1.21	1.00	6.096 5(1)	56.65	3.0(2)	2.9(4)	0.280(1)	0.245(2)
628	1–5	1.19	1.00	6.099 1(1)	56.72	2.9(1)	3.1(4)	0.281(1)	0.245(2)
633	1–5	1.29	1.00	6.100 5(1)	56.76	2.9(1)	3.3(4)	0.281(1)	0.246(2)
638	1–5	1.24	1.00	6.101 5(1)	56.79	3.3(1)	3.5(5)	0.281(1)	0.246(2)
641	1–30	1.47	1.00	6.102 65(8)	56.82	3.01(8)	3.9(3)	0.282(1)	0.246(1)
643	1–10	1.46	0.71(7)	6.103 0(1)	56.83	3.2(1)	3.6(5)	0.280(2)	0.241(2)
643	11–20	1.55	0.45(5)	6.103 0(2)	56.83	3.1(3)	3.0(7)	0.280(2)	0.240(3)
643	21–30	1.54	0.45(5)	6.103 0(2)	56.83	3.0(3)	3.2(7)	0.279(2)	0.238(3)

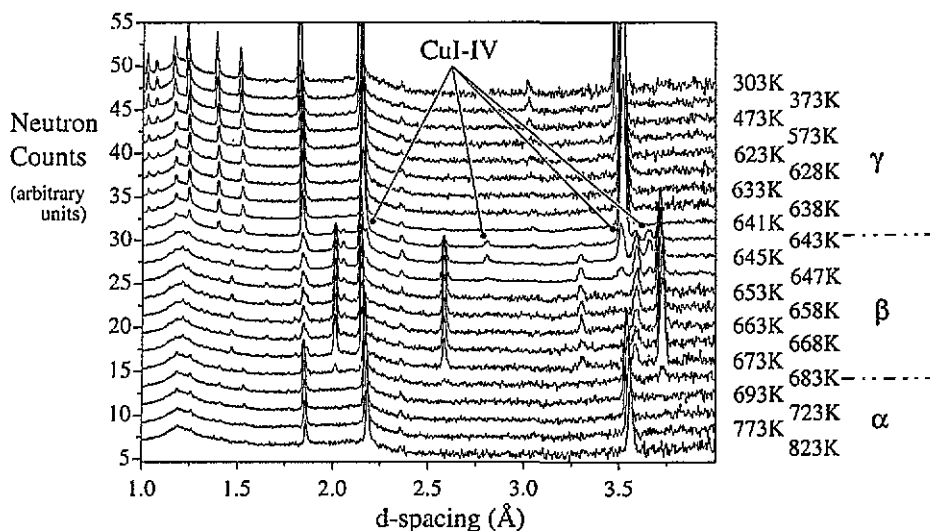


Figure 1. Plot of powder diffraction patterns from CuI at all measured temperatures. Data are from the  $2\theta \sim 90^\circ$  detector banks on Polaris. The changes at the  $\gamma \rightarrow \beta$  and  $\beta \rightarrow \alpha$  phase transitions can be clearly seen, as can certain anomalous peaks within the  $\beta$ -phase, attributed to CuI-IV.

### 3.1. $\gamma$ -CuI

The ambient temperature  $\gamma$ -CuI phase possesses the zinc blende structure (space group  $F\bar{4}3m$ ) with  $\text{I}^-$  in 4(a) sites at (0, 0, 0) etc and  $\text{Cu}^+$  in 4(c) sites at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  etc. It is well known that  $\gamma$ -CuI displays increased anharmonicity of the  $\text{Cu}^+$  thermal vibrations as temperature increases, which can be satisfactorily modelled by 'splitting' the 4(c) sites into partially occupied 16(e) sites at ( $x, x, x$ ) etc, with  $x \sim 0.29$  [5].

The results of the refinements of the structure of  $\gamma$ -CuI are summarized in table 1.

The anharmonicity of the  $\text{Cu}^+$  ion is clearly observed to increase with temperature, with the  $x$  positional parameter for the partially occupied 16(e) sites becoming progressively larger than  $\frac{1}{4}$ . However, initial refinements based on this simple structural model gave a marginally poorer  $\chi^2$  value at higher temperatures which may, in part, be due to the inadequacy of the 16(e) 'split site' model to account for the anharmonic thermal vibrations. Attempts to 'split' the  $\text{Cu}^+$  site in  $\langle 001 \rangle$  rather than  $\langle 111 \rangle$  directions using 24(g) sites proved unsuccessful, leading to unstable refinements. The direction of  $\text{Cu}^+$  disorder is, therefore, in  $\langle 111 \rangle$  towards the faces of the surrounding  $\text{I}^-$  tetrahedra which supports the theories that conduction takes place via octahedral sites [8]. However, constrained refinements with a variable fraction of  $\text{Cu}^+$  located on the octahedral 4(b) sites at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  etc proved unstable, showing that this position is not a stable energy minimum.

The increased ionic conductivity observed in  $\gamma$ -CuI below the  $\gamma \rightarrow \beta$  transition suggests that a significant number of cations undergo diffusion over relatively long distances. This is supported by refinements with variable occupancy of the 16(e) sites and the remaining  $\text{Cu}^+$  on the alternative 16(e) set of tetrahedral sites at  $(x, x, x)$  etc with  $x \sim \frac{3}{4}$ , which gave a slightly better fit to the data. Approximately 4% of  $\text{Cu}^+$  ions are found to be located on these 16(e) interstitial tetrahedral sites at the highest temperatures just below the  $\gamma$ - $\beta$  phase boundary.

### 3.2. $\beta$ -CuI

Keen and Hull [1] describe the structure of  $\beta$ -CuI in space group  $P\bar{3}m1$ , with  $\text{I}^-$  in 2(d) sites at  $(\frac{1}{3}, \frac{2}{3}, z)$  and  $(\frac{2}{3}, \frac{1}{3}, \bar{z})$  with  $z = 0.242(1)$  and the  $\text{Cu}^+$  ions 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  $z = 0.8786(8)$ . Table 2 summarizes the results of the structural refinements of the diffraction data collected from the  $\beta$ -phase of CuI, using the above  $P\bar{3}m1$  structure. The  $c$  axis is seen to contract and the  $a$  axis expand with increasing temperature, such that the  $c/a$  ratio reduces towards the close-packed 'ideal' value of 1.633. The increased  $\text{Cu}^+$  ion occupation with temperature of 2(d) sites with  $z \sim 0.88$  reported in Keen and Hull [1] is not seen convincingly here, although the amount of disorder is about the same. This discrepancy is attributed to the coexistence of the transient rhombohedral phase at the lower temperatures in this measurement, with consequent overlap of reflections in the multiphase refinements (see below), which was not present in [1].

### 3.3. $\alpha$ -CuI

Refinements of this phase were based on  $Fm\bar{3}m$  symmetry and are summarized in table 3. These results illustrate the considerable anharmonicity of the  $\text{Cu}^+$  thermal vibrations which can be modelled by random occupation of 32(f) sites at  $(x, x, x)$  etc, with  $x \sim 0.3$ . Attempts were made to refine the data with a fraction of cations occupying octahedral 4(b) sites at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  etc, or with the 8(c) sites at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  etc splitting into 48(g) sites at  $(x, \frac{1}{4}, \frac{1}{4})$  etc ( $\text{Cu}^+$  ion disordering in  $\langle 100 \rangle$  directions) or with a non-random occupation of the possible tetrahedral sites. The latter is equivalent to a highly disordered  $\gamma$ -phase, with a different proportion of  $\text{Cu}^+$  in 16(e) with  $x \sim 0.3$  than in 16(e) with  $x \sim 0.7$  using  $F43m$  symmetry. All these models were either unstable due to excessive correlations between fitted parameters or produced a poorer fit to the data. The temperature factors and  $x_{\text{Cu}}$  are all larger than in  $\gamma$ -CuI, showing the increased ionic disorder in this phase. The direction of  $\text{Cu}^+$  ion disorder is still towards the faces of the  $\text{I}^-$  tetrahedra, although even in this phase with high ionic conductivity no  $\text{Cu}^+$  ions are found to occupy octahedral 4(b) sites. At the highest temperatures, just below  $T_M$ , the material is highly disordered, such that only three Bragg peaks are clearly observed (see figure 1).

**Table 2.** Structural parameters of  $\beta$ -CuI in the temperature range 643–683 K.  $\beta$ -CuI; Space group:  $P\bar{3}m1$ ; Atom positions: I in 2(d) at  $(\frac{1}{3}, \frac{2}{3}, z_1)$  and  $(\frac{2}{3}, \frac{1}{3}, \bar{z}_1)$ , CuI in 2(d) at  $(\frac{1}{3}, \frac{2}{3}, z_{CuI})$  and  $(\frac{2}{3}, \frac{1}{3}, \bar{z}_{CuI})$ , 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  $B_I$ ,  $B_{CuI}$  and  $B_{Cu2}$ ; Positional parameters  $z_1$ ,  $z_{CuI}$  and  $z_{Cu2}$ ; Site occupancies  $n_{CuI}$  and  $n_{Cu2}$ ; Parameter constraints:  $B_{Cu2} = B_{CuI}$ ,  $z_{Cu2} = \frac{1}{2} - z_{CuI}$  and  $n_{Cu2} = 1 - n_{CuI}$ .

T (K)	No runs	$\chi^2$	$V_{fraction}$	a (Å)	c (Å)	c/a ratio	V/Z (Å <sup>3</sup> )	$B_I$ (Å <sup>2</sup> )	$B_{CuI}$ (Å <sup>2</sup> )	$z_1$	$z_{CuI}$	$n_{CuI}$
643	1–10	1.46	0.25(2)	4.290(2)	7.191(6)	1.676	57.30	7(1)	11(2)	0.25(1)	0.656(5)	0.69(9)
643	11–20	1.55	0.28(2)	4.292(3)	7.192(4)	1.676	57.37	4.8(9)	10(2)	0.237(6)	0.637(4)	0.70(4)
643	21–30	1.54	0.28(2)	4.291(2)	7.193(4)	1.676	57.35	5.1(9)	9(2)	0.252(9)	0.641(4)	0.76(5)
645	1–10	1.66	0.641(4)	4.292(1)	7.192(2)	1.676	57.36	5.0(4)	10.8(7)	0.241(4)	0.638(2)	0.73(3)
645	11–20	1.55	0.723(3)	4.291(1)	7.193(2)	1.676	57.36	4.7(3)	11.4(6)	0.244(3)	0.634(2)	0.78(2)
645	21–30	1.66	0.839(2)	4.2919(8)	7.192(1)	1.676	57.37	4.9(3)	11.3(5)	0.244(3)	0.632(1)	0.79(2)
647	1–10	1.56	0.826(3)	4.2925(7)	7.192(1)	1.675	57.38	4.3(2)	9.8(5)	0.242(2)	0.626(2)	0.84(1)
647	11–20	1.58	0.92(2)	4.2933(3)	7.1912(6)	1.675	57.40	4.9(2)	10.8(4)	0.243(2)	0.628(1)	0.82(1)
647	21–30	1.47	0.859(4)	4.2932(6)	7.192(1)	1.675	57.40	4.6(2)	9.7(4)	0.242(2)	0.624(1)	0.84(1)
653	1–5	1.19	0.984(5)	4.2958(5)	7.191(1)	1.674	57.46	4.8(3)	11.1(5)	0.244(3)	0.625(2)	0.83(2)
658	1–5	1.35	1.00	4.2994(5)	7.187(1)	1.672	57.53	5.0(3)	11.8(5)	0.249(3)	0.629(1)	0.81(2)
663	1–5	1.24	1.00	4.3024(5)	7.186(1)	1.670	57.59	4.9(3)	12.9(6)	0.247(3)	0.626(2)	0.82(2)
668	1–5	1.21	1.00	4.3055(5)	7.183(1)	1.668	57.66	4.8(3)	12.1(6)	0.248(3)	0.625(2)	0.79(2)
673	1–5	1.25	0.89(1)	4.3089(2)	7.1789(6)	1.666	57.71	5.2(3)	11.6(7)	0.250(3)	0.625(2)	0.79(2)
683	1–5	1.28	0.37(6)	4.3123(7)	7.177(1)	1.664	57.79	10(3)	27(7)	0.250	0.625	0.79

### 3.4. The Transient Phase (CuI-IV)

On first heating through the  $\gamma \rightarrow \beta$  transition during the measurement made on HRPD [1] data were collected at  $T = 653$  K of another phase, which contained reflections which could not be indexed on any of the  $\alpha$ -,  $\beta$ - or  $\gamma$ -phases, and did not contain reflections which are strong in these phases (figure 2). This indicates that an additional phase is present rather than a distortion of one of the known phases. The observed reflections could all be indexed on a rhombohedral unit cell with  $a = 4.298\,50(1)$  Å and  $c = 21.4668(9)$  Å in the hexagonal description. Both the cell parameters and the general distribution of the intensities of the Bragg intensities were observed to be similar to those measured recently for the high-pressure phase CuI-IV at 1.74 GPa and ambient temperature [13]. As a result, the starting model for the fit to the high-temperature data was taken to be that of CuI-IV. The latter can be described as a distorted FCC arrangement of  $I^-$  ions, with the  $Cu^+$  ions distributed in tetrahedral sites. Refinements with this model gave a good fit with  $\chi^2 = 1.01$  ( $R_w = 8.82\%$  and  $R_{exp} = 8.78\%$ ).

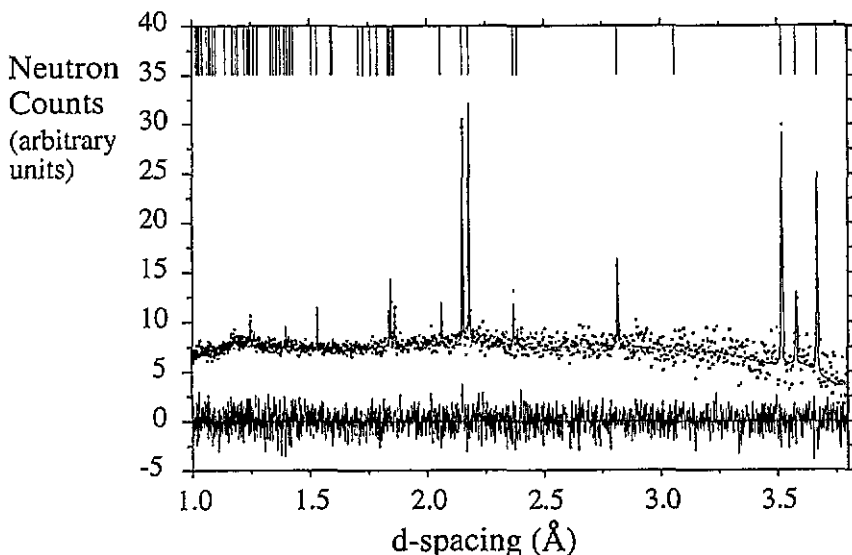
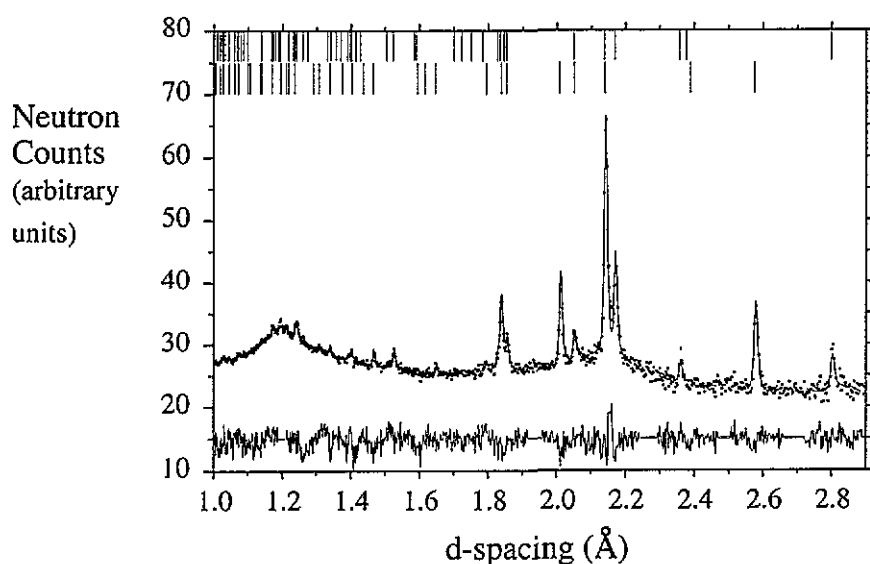


Figure 2. Powder diffraction pattern from CuI-IV at 653 K measured on HRPD. Points are normalized experimental data, the line through the points is the refined profile, and the lower plot is the difference divided by experimental standard deviation. Tick marks at the top of the plot show the calculated positions of the CuI-IV peaks.

The data were collected for a relatively short time ( $\sim 15$  min) before the temperature was raised further, after which the phase was not stabilized again on subsequent heating through the  $\gamma \rightarrow \beta$  transition. The poor statistical quality of the powder diffraction pattern (figure 2), which is reflected in the fairly high  $R_w$ , made it unrealistic to consider disordering the  $Cu^+$  ions over other possible tetrahedral sites, or to consider anharmonicity. This structure has a volume per CuI formula unit ( $V/Z$ ) of  $57.25$  Å<sup>3</sup>, mid-way between those found in the  $\gamma$ - and  $\alpha$ -phases. The  $c/a$  ratio of 1.6647 (taking into account the tripled hexagonal  $c$  axis used to describe the rhombohedral unit cell) is lower than those found in  $\beta$ -CuI (section 3.2).

**Table 3.** Structural parameters of  $\alpha$ -CuI in the temperature range 673–823 K.  $\alpha$ -CuI; Space group:  $Fm\bar{3}m$ ; Atom positions: I in 4(a) at (0,0,0) etc, CuI in 32(f) at ( $x_{Cu}$ ,  $x_{Cu}$ ,  $x_{Cu}$ ) etc; Refined parameters: Isotropic thermal parameters  $B_I$  and  $B_{Cu}$ , Cu positional parameter  $x_{Cu}$ ; Parameter constraints: Cu site occupancy  $n_{Cu} = \frac{1}{8}$ .

$T$ (K)	$\chi^2$	$V_{\text{fraction}}$	$a$ (Å)	$V/Z$ (Å <sup>3</sup> )	$B_I$ (Å <sup>2</sup> )	$B_{Cu}$ (Å <sup>2</sup> )	$x_{Cu}$
673	1.25	0.11(4)	6.134(2)	57.69	6(3)	6(6)	0.31(1)
683	1.28	0.6(2)	6.1361(2)	57.76	4.8(2)	7.3(8)	0.297(2)
693	1.26	1.00	6.1397(2)	57.86	5.1(2)	7.4(8)	0.298(1)
723	1.27	1.00	6.1480(2)	58.09	5.5(3)	9(1)	0.300(2)
773	1.20	1.00	6.1623(3)	58.50	6.5(4)	10(1)	0.305(2)
823	1.15	1.00	6.1753(4)	58.87	8.1(9)	11(3)	0.308(2)



**Figure 3.** Powder diffraction pattern from mixed phase CuI-IV and  $\beta$ -CuI at 645 K measured on Polaris. Points are normalized experimental data, the line through the points is the refined profile, and the lower plot is the difference divided by experimental standard deviation, offset vertically by 15. Tick marks at the top of the plot show the calculated positions of CuI-IV (upper) and  $\beta$ -CuI (lower) peaks. The relatively poor fit around 2.16 Å arises from a remnant of the (220) reflection of  $\gamma$ -CuI.

The measurements made on Polaris, to confirm the existence of this phase, failed to obtain it as a single phase, but it was observed together with  $\beta$ -CuI (and also with  $\gamma$ -CuI at 643 K) in both measured samples (see for example the refined powder pattern in figure 3). It was present between 643 K and 650 K in varying proportions (see table 4). The careful heating carried out in these measurements should give a more reliable picture of the coexistence of this phase with  $\beta$ -CuI, rather than the 'one-off' observation on HRPD. Phase IV appears at the same temperature as  $\beta$ -CuI appears, but by 645 K the proportion of CuI-IV had decreased, and continued to decrease such that in the 30 five minute runs at this temperature, the volume percentages of phase IV refined from runs 1–10, 11–20 and 21–30 were 36(4), 28(3) and 16(2)% respectively. At 647 K the proportions for the equivalent time intervals were 17(4), 8(2) and 14(4)%, with only a few per cent at 653 K. Hence there



is slow conversion from IV to  $\beta$ , although it appears that temperature must be raised for complete conversion.

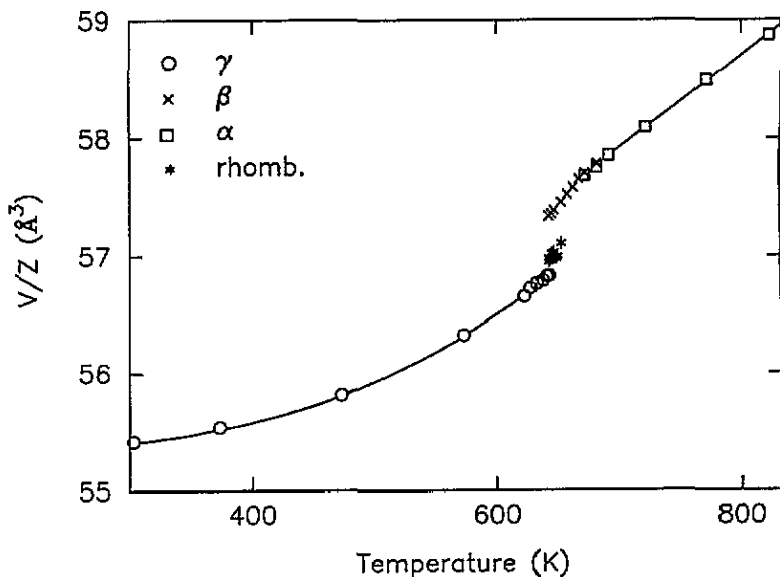


Figure 4. The unit cell volume per formula unit ( $V/Z$ ) of CuI as a function of temperature determined from powder neutron diffraction. The errors on the values are comparable with the size of the symbols.

#### 4. Discussion

Figure 4 shows the volume per CuI formula unit ( $V/Z$ ) as a function of temperature within the various phases. There is a clear upturn in the curve while still within the  $\gamma$ -phase, whereas the volume change with temperature is linear in  $\alpha$ -CuI. There is a 0.8% volume change at the  $\gamma \rightarrow \beta$  phase transition,  $V/Z$  is larger in  $\beta$ -CuI than in phase IV and there is no significant change in cell volume at the  $\beta \rightarrow \alpha$  phase transition. The thermal expansion of the copper halides has been investigated by Plendl and Mansur [14] below room temperature. They found a linear relationship between lattice parameter and temperature for  $\gamma$ -CuI in the temperature range  $\sim 80 \text{ K} < T < 300 \text{ K}$ , with a thermal expansion of  $\sim 1 \times 10^{-4} \text{ \AA K}^{-1}$ . The anomalous increase in cell volume just below the  $\gamma$ - $\beta$  phase boundary (figure 4) is indicative of the onset of  $\text{Cu}^+$  ion disorder. This confirms what has been observed in specific heat measurements [4, 15] where, as well as observing two clear transitions at the  $\gamma \rightarrow \beta$  and  $\beta \rightarrow \alpha$  phase boundaries, a gradual increase in signal was seen well below the  $\gamma \rightarrow \beta$  phase transition temperature and the ' $\gamma \rightarrow \alpha$ ' transition was considered second order. Indeed the type of disorder which occurs in  $\gamma$ -CuI, whereby  $\text{Cu}^+$  ions begin to move from 16(e) sites with  $x \sim 0.28$  to 16(e) sites with  $x \sim 0.72$ , is suggestive of the beginnings of transformation to  $\alpha$ -CuI where  $\text{Cu}^+$  ions are randomly distributed between '16(e) sites' ( $F\bar{4}3m$  description) with  $x \sim 0.3$  and  $x \sim 0.7$ .

This paper reports the first observation of CuI-IV at ambient pressure. In part this has been made possible because of rapid data collection, high temperature stability and the



possibility of multiphase refinement. Previous work has often had difficulty in stabilizing  $\beta$ -CuI without contamination from the neighbouring  $\gamma$ - and  $\alpha$ -phases [7]. In retrospect it is possible that some of these problems were due to the presence of CuI-IV. The  $p$ - $T$  phase diagram based on DTA measurements [16] shows only a tentative boundary between the  $\beta$ -CuI and CuI-IV at  $\sim 2.1$  kbar. These diffraction measurements vindicate this uncertainty since  $\beta$ -CuI and CuI-IV have been found to coexist at ambient pressure. It must be concluded that  $\beta$ -CuI has a more stable structure than CuI-IV in order for it to exist at all, since the transformation  $\gamma \rightarrow \text{IV} \rightarrow \alpha$  would only involve a minimal rearrangement of the  $\text{I}^-$  ion sublattice within an FCC framework and would be a much more logical transition route between  $\gamma$ - and  $\alpha$ -CuI if one were required at all. The evidence of these measurements however does not suggest that CuI-IV is an intermediary for the  $\gamma \rightarrow \beta$  phase transition;  $\beta$ -CuI appears simultaneously with CuI-IV at the  $\gamma \rightarrow \beta$  phase boundary and the refined volume fractions imply direct  $\gamma \rightarrow \beta$  conversion.

The ionic conductivity can be considered simply in terms of the number of defects in each phase and their ability to move through the lattice. In  $\gamma$ -CuI there are  $\sim 4\%$  of  $\text{Cu}^+$  ions at the highest temperatures. This rises sharply in the  $\beta$ -phase where there are  $\sim 10\%$ , increasing to  $\sim 20\%$  just below the  $\beta \rightarrow \alpha$  phase boundary [1].  $\alpha$ -CuI has a completely disordered  $\text{Cu}^+$  ion distribution within the available tetrahedral voids and hence can be considered to have 50% defect  $\text{Cu}^+$  ions. There is also a large increase in anharmonicity of the mobile  $\text{Cu}^+$  ions. Figure 5 shows the distance  $\text{Cu}^+$  ions vibrate away from their ideal 4(c) sites ( $\gamma$ -phase) or 8(c) sites ( $\alpha$ -phase) in  $\langle 111 \rangle$  directions away from nearest-neighbour  $\text{I}^-$  ions as a function of temperature. This is determined as the sum of the root mean squared (rms) distance and the displacement of the site from its undistorted position, i.e.  $[(B_{\text{Cu}}/8\pi^2)^{1/2}]/a + \sqrt{3}(x_{\text{Cu}} - \frac{1}{4})$ . This curve, which is normalized to the lattice parameter,  $a$ , still turns upwards slightly in the  $\gamma$ -phase, has a large rise at the ' $\gamma \rightarrow \alpha$ ' phase boundary and a linear behaviour in the  $\alpha$ -phase. The anharmonicity in  $\gamma$ -CuI only extends  $\sim 0.09a$  ( $\sim 0.55\text{\AA}$ ) away from the tetrahedron centre towards the tetrahedron faces just below the  $\gamma \rightarrow \beta$  phase boundary (figure 5). The faces of the  $\text{I}^-$  tetrahedron, which provide the lowest energy barrier to  $\text{Cu}^+$  motion, are  $0.1443a$  from their centre. Only a small proportion of ions have a sufficiently large amplitude of vibration (or energy) to penetrate the  $\text{I}^-$  tetrahedra faces and move, via octahedral voids, into neighbouring tetrahedral sites. In  $\alpha$ -CuI the  $\text{Cu}^+$  ions have an rms distance in  $\langle 111 \rangle$  directions of  $\sim 0.15a$  and therefore many more ions can pass through the  $\text{I}^-$  tetrahedron faces, contributing to conduction. In  $\beta$ -CuI some tetrahedral sites are much closer, and the  $\text{I}^-$  sublattice is distorted and swollen relative to the  $\gamma$ - and  $\alpha$ -phases. Two sites are  $\sim 1.8\text{\AA}$  apart, separated by an undistorted tetrahedral face of  $\text{I}^-$  ions, perpendicular to the  $c$  axis. The next-nearest tetrahedral sites are further away, but since the  $\text{I}^-$  sublattice is distorted, motion may also take place between these sites. The close proximity of the 2(d) sites allows easy disordering between them. The temperature-dependent increase in cell volume, increased thermal motion of ions and increased occupation of interstitial sites are all factors in the increase of ionic conduction with raised temperature.

It is perhaps curious, given the accepted conductivity mechanism of  $\text{Cu}^+$  ion motion in  $\langle 111 \rangle$  directions from tetrahedral through octahedral to tetrahedral voids in the  $\text{I}^-$  sublattice of  $\gamma$ - and  $\alpha$ -CuI, that no occupancy of octahedral sites can be observed. This observation can be contrasted with EXAFS results which give significant occupation of octahedral sites [17]. It should also be noted that certain studies have asserted that  $\text{Cu}^+$  ion mobility is also likely in  $\langle 100 \rangle$  directions through the tetrahedral edges, in particular MD simulation studies [18] and Mössbauer scattering [19]. It is also suggested by Yude *et al* [7]. Such conduction pathways would require no occupation of octahedral sites.

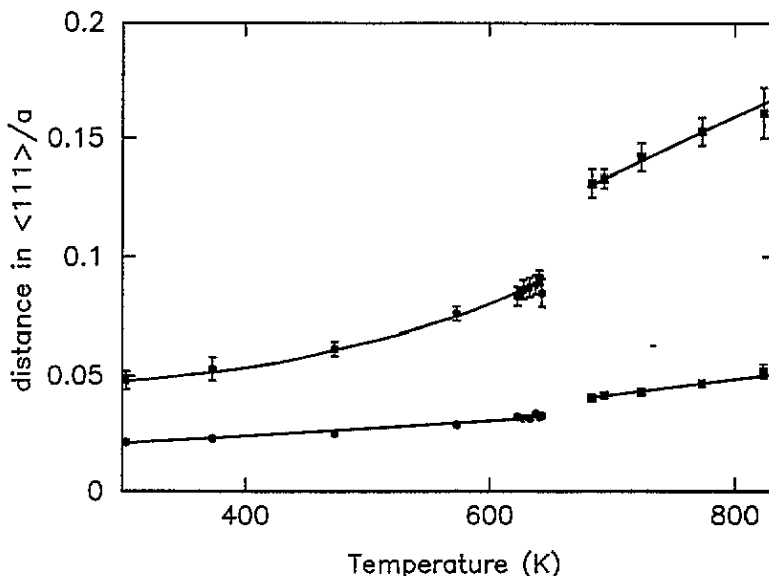


Figure 5. The average distance a  $\text{Cu}^+$  ion in CuI vibrates away from its ideal 4(c) site ( $\gamma$ -CuI, ●) or 8(c) site ( $\alpha$ -CuI, ■) in (111) directions towards the face centres of the surrounding I-tetrahedron as a function of temperature (upper curve). For comparison, the lower curve shows the equivalent distances  $\text{I}^-$  ions vibrate from their ideal sites.

## 5. Conclusions

The detailed powder diffraction studies described in this paper have shown that a small increase in disorder occurs within the  $\gamma$ -phase of CuI, prior to the transformation to the  $\beta$ -phase. This disorder could be considered as a precursor to a continuous transformation directly into the  $\alpha$ -phase.  $\beta$ -CuI displays a slight distortion away from ideal hexagonal close packing, which reduces with increasing temperature accompanied by disordering of  $\text{Cu}^+$  ions between the available tetrahedral sites. The formation of  $\alpha$ -CuI results in no change of cell volume and, in contrast with some previous work, no occupation of octahedral sites.  $\alpha$ -CuI has a random  $\text{Cu}^+$  ion occupation over all the available tetrahedral sites, which was initiated in  $\gamma$ -CuI. The development of disorder with temperature in the three structures is consistent with ionic conductivity measurements. CuI phase IV has been observed for the first time at ambient pressure. It exists in a similar temperature range to that of  $\beta$ -CuI and eventually transforms to  $\beta$ -CuI.

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