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The Thermal Expansion of Silver Iodide and the Cuprous Halides

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The expansions of silver iodide and the cuprous halide salts have been investigated by powder X-ray techniques. Measurements have been made between −190 °C and the respective melting points. The 'anomalous' expansion behaviour of these halides, in particular the negative expansion of β-AgI, is discussed in terms of specific models of Frenkel disorder.

Introduction

In contrast to the extensive studies performed on AgBr and AgCl little effort has been made to understand the nature of structural disorder in AgI, CuCl, CuBr and CuI. This is primarily a consequence of the comparative structural simplicity of AgCl and AgBr, as Table 1 illustrates. Intrinsic thermal disorder in AgBr and AgCl has been previously discussed (Lawn, 1963*a*) and appears to be predominantly Frenkel with 'mixed' Frenkel and Schottky types at high temperatures. Most evidence, particularly the ionic transport phenomena (see for example Lidiard, 1957), does in fact appear to favour the Frenkel model in all silver and cuprous halides.

Table 1. *Crystal structures of silver and cuprous halides*

Substance	Modification	Structure*	Region of stability
AgCl		*B*1	Below T_m
AgBr		*B*1	Below T_m
AgI	α	*B*23(aver.)	150 °C–T_m
	β	*B*4	<150 °C
	γ	*B*3	<150 °C
	high-pressure	*B*1	>3020 atm
CuCl	β	*B*4(aver.)	435 °C–T_m
	γ	*B*3	<435 °C
CuBr	α	*B*23(aver.)	485 °C–T_m
	β	*B*4(aver.)	405 °C–485 °C
	γ	*B*3	<405 °C
CuI	α	*B*3(aver.)	430 °C–T_m
	β	*B*4(aver.)	390 °C–430 °C
	γ	*B*3	<390 °C

* Structure designation follows from *Structure Reports*. (aver.) denotes 'averaged' structure and T_m melting point.

The origin of the negative expansion coefficient observed in hexagonal β-AgI has yet to be unequivocally established. The theories of Barron (1955) and Blackman (1958), based on the fundamental vibrating lattice model, allow for negative coefficients at low temperatures ($0\cdot2$–$0\cdot3\Theta$, Θ = Debye temperature). Such behaviour is indeed characteristic of many materials possessing 'open' (diamond, *B*3, *B*4) structures (*e.g.* Gibbons, 1958; Novikova & Strelkow, 1959; Novikova, 1960*a*, *b*, *c*, 1961). However, the expansion of β-AgI (Lieser, 1955) is of a different nature, featuring an increasing contraction from −180 °C to the β–α transition at 150 °C. Lieser (1954, 1955, 1956*a*, *b*, *c*, 1958) points out that thermal disorder, which accounts for many 'defect-sensitive' properties of AgI over the same temperature range, may be the cause of such a contraction. He presents a Frenkel model consistent with all properties examined.

Table 2. *Comparison of mean linear expansion coefficient* ($\times 10^6$) *between* 20 °C *and* 120 °C *for cuprous halides*

	Klemm *et al.* (1928)	Present work
γ-CuCl	10	17
γ-CuBr	19	17
γ-CuI	22	19

The meagre expansion data available on the cuprous halides are limited to mean linear expansion coefficients measured between 20 °C and 120 °C (Table 2) by Klemm, Tilk & Mullenheim (1928). Since the structures and ionic transport properties of these compounds bear a striking resemblance to those of AgI, one may also expect parallel expansion behaviour. However, it will be seen that such is not the case, which indicates that the respective defect mechanisms are not identical.

Unit-cell dimensions of the AgI, CuCl, CuBr and CuI polymorphs have been recorded over a wide temperature range on high- and low-temperature X-ray powder cameras. Their collation and subsequent analysis follow the procedures outlined in a previous paper (Lawn, 1963*a*). The expansion characteristics are found to be consistent with Frenkel defects.

Experimental

Silver iodide powder was initially precipitated from solutions of analytical reagent grade silver nitrate and

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potassium iodide. Cubic (γ) and hexagonal (β) modifications were then prepared separately by redissolving the powder in saturated solutions of silver nitrate and potassium iodide respectively (Kolkmeijer & van Hengel, 1934) and reprecipitating by gradual dilution. However, in no instance could a 'pure' structural type be isolated completely, at least one reflexion of the sister modification appearing on each X-ray pattern exposed. Various other methods of preparation and treatment (Majumdar & Roy, 1959) were attempted but to no further avail. Particular caution had therefore to be exercised since the modifications produce powder patterns with many overlapping reflexions.

Samples of cuprous chloride (from A. R.) and cuprous bromide and cuprous iodide (from technical grade reagents) were prepared in a manner similar to that described by the U.S. National Bureau of Standards (1954).

The powders (β-AgI excepted) were crushed, encased and vacuum-sealed into 0·5 mm bore silica glass capillaries (high-temperature camera) and 0·3 mm Lindemann glass capillaries (low-temperature camera). All but γ-AgI were annealed below their respective transition temperatures for several hours. (The foregoing treatment afforded AgI proved necessary since the β and γ phases exist under equilibrium and non-equilibrium conditions respectively.) Spectroscopic analyses suggest maximum impurity levels of $<0{\cdot}05\%$ in any one specimen.

The previously mentioned high- and low-temperature X-ray powder units recorded lattice parameters of each halide at several temperatures. Taking as a criterion the quality of the back-reflexion photograph, unfiltered Ni K radiation proved generally most useful, although other targets were occasionally substituted. Most halides examined gave clear room temperature patterns with an α_1 line above $\theta=80°$. Silver iodide provided the exception with diffuse back-reflexion lines and high background intensity. Deterioration of pattern quality with temperature was not particularly noticeable for the γ polymorphs but most β and α polymorphs produced such inferior patterns as a result of rapid recrystallization that a comprehensive examination was impossible.

Line positions on the films were measured by means of a sliding vernier scale capable of reproducing high quality reflexions to within $\pm 0{\cdot}02$ mm.

Expansion data

A weighted least-squares procedure involving an extrapolation against the Nelson–Riley function to $\theta=90°$ was adopted to compute lattice parameters of all cubic modifications. Hexagonal unit-cell lengths were similarly derived with the use of a slightly modified scheme which weights individual reflexions according to their h, k, l indices (Lawn, 1963b). The calculations were coded in FORTRAN II language for solution on an IBM 1620 digital computer. The resulting lattice parameters (corrected for refraction)

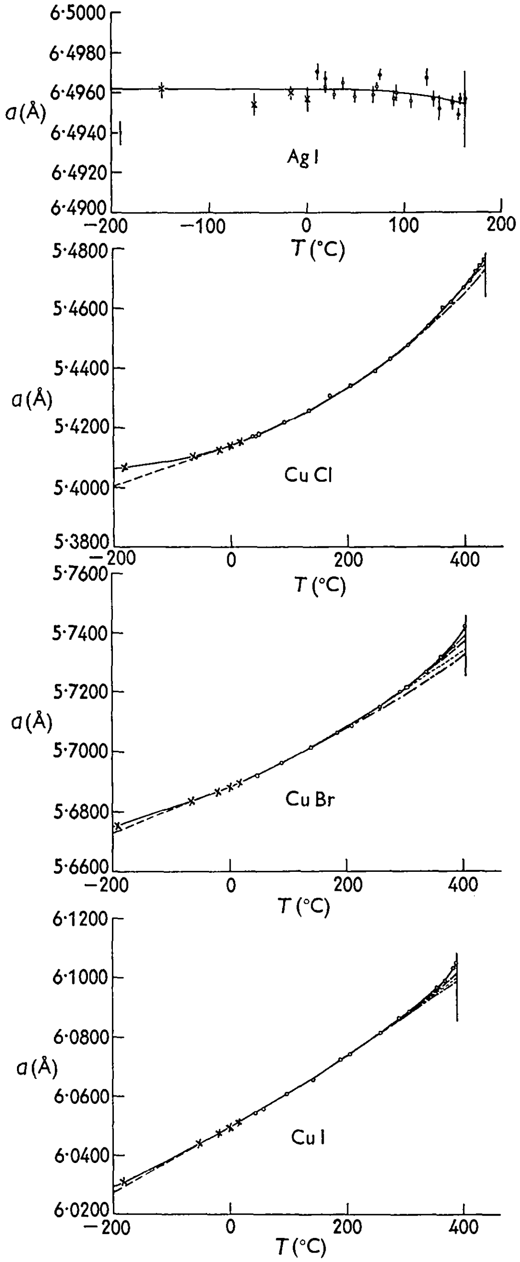

Fig. 1. Lattice parameters against temperature for the γ polymorphs.

○ High-temperature unit × Low-temperature unit

- - - - - - - - - - - - - -	Lawson
— – — – — – — – —	Fischmeister
— — — — — — — —	Merriam *et al.*
——— ———	Laval

For CuI the 'Laval' and 'Merriam plots' coincide. The dashed line below room temperature illustrates the Fischmeister approximation at lower temperatures: note the poor agreement with experiment.

are shown as a function of temperature in Figs. 1–3. Wherever the standard error of an observation is greater than the size of the indicating circle or cross on the diagrams it is accordingly illustrated. Only with β- and γ-AgI does the scatter of observations significantly exceed the standard errors of the parameters, indicating some hitherto unconsidered source of systematic error inherent in these polymorphs.

The expansion trend of the cuprous halides is seen to be of a different nature from that of AgI. Lieser's (1955) AgI macroscopic and X-ray expansion curves (calculated in conjunction with Cohen & Dobbenburgh's (1928) densities of β- and α-AgI at 150 °C) are illustrated in Figs. 2 and 3. Lieser's and the present X-ray curves do not agree within the range of the error limits cited. However, agreement is sufficient to dispel any prospect of appreciable Schottky disorder. The greatest deviation of any one X-ray-determined observation from the Lieser macroscopic curves is equivalent to 0·1 mol.% Schottky defects in α-AgI (compare 0·2% Lieser), as computed from the well established relationship:

$$(n/N)_s = \delta V/V = 3\,.\,\delta a/a$$

where $(n/N)_s$ is the number of Schottky defects formed per ion pair and δV (or δa) the separation between the macroscopic and X-ray expansion curves. In β-AgI $(n/N)_s$ is found to be considerably smaller. Such small concentrations cannot account for the prominent 'structure-sensitive' properties exhibited by AgI. Schottky defects are therefore of only secondary importance, especially in α-AgI where the 'averaged' structure consists of nearly 100% Frenkel disorder in the silver partial lattice (Strock, 1935).

No satisfactory macroscopic data are available in the literature for comparison with the present X-ray data on γ-AgI or the cuprous halides. However, the expansions of β- and γ-AgI show similar trends (Fig. 7) and X-rays diffracted by polycrystalline samples of AgI and cuprous halides reveal the same intensity anomalies (Hoshino, Miyake & Takenaka, 1952; Hoshino, 1952, 1957; Hoshino & Miyake, 1958). These substances also reveal similar ionic transport and polymorphic characteristics. It is therefore tacitly assumed in the following that the defect mechanism is basically the same (Frenkel) in all silver and cuprous halide crystals.

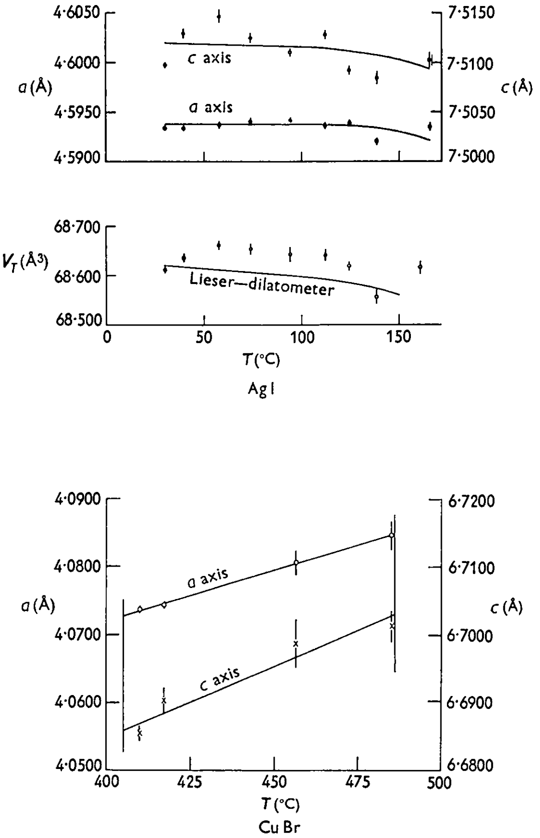

Fig. 2. Lattice parameters against temperature for the β polymorphs (hexagonal symmetry). (Data on β-CuCl and β-CuI are restricted — see Fig. 7.) Lieser's β-AgI data are represented by the smoothed curve in the molecular volume (V_T) *versus* temperature graph.

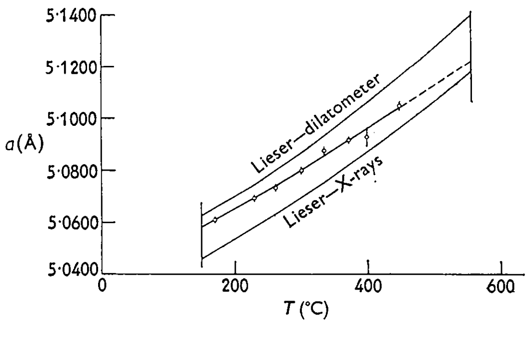

Fig. 3. Lattice parameters against temperature for α-AgI. Included are Lieser's smoothed experimental data.

The 'anomalous' expansion

The 'anomalous' expansion is estimated simply by subtracting the calculated defect-free-lattice ('normal') contribution from the observed expansion. All determinations of the 'normal' expansion involve an extrapolation of data from low temperatures where the behaviour is regular. Since no such region of regular expansion has been observed for β- or γ-AgI the treatment is not extended to these particular polymorphs. All polymorphs with 'averaged' structures are also disregarded here since their defect structure is little affected by temperature.

Accordingly, the following established techniques are confined to the γ modifications of CuCl, CuBr and CuI, adopting the γ–β transition as a crude melting point:

(i) After Lawson (1950), included mainly for historical interest. The 'normal' expansion coefficient is assumed to be constant above T_0, the 'knee' temperature in conductivity experiments, where thermal disorder predominates over all other crystal imperfections. From inflexions on the conductivity curves of Wagner & Wagner (1957) one obtains $T_0 \sim 260$ °C (γ-CuBr) and ~ 270 °C (γ-CuI). There is much uncertainty associated with the estimation of T_0: in fact no inflexion is apparent for γ-CuCl.

(ii) After Fischmeister (1956*a*, *b*). The expansion of a defect-free lattice is estimated from Gruneisen theory. Insensitivity of this method makes the selection of the 'normal' expansion susceptible to error, especially as the 'anomalous' effect in the cuprous halides is small (as compared with that in the silver halides, say).

(iii) After Merriam, Smoluchowski & Wiegand (1962). Above T_0 the expansion coefficient α is extrapolated as a linear function in temperature (high-temperature approximation to the Gruneisen equation). The 'anomalous' expansion is found to be considerably less sensitive here to the selection of the 'normal' contribution than in the 'Fischmeister procedure'.

The corresponding 'normal' expansions are illustrated on the lattice parameter–temperature graphs.

The theory of thermal dilatation developed by Laval (1961*a*, *b*) provides a possible fourth method of analysis. Robbrecht, Jacobs & Iserentant (1962) find the expansion of copper more satisfactorily explained by this theory than by customary Gruneisen theory. Complexity of the mathematics and lack of crystal data together preclude a rigorous application of his formulation here. However, expansion behaviour may be conveniently followed on a $\alpha' = d\alpha/dT$ *versus* T plot (Laval, 1961*b*, Fig. 6). Laval finds α' approximately invariant with T at intermediate temperatures and proportional to T as the 'melting point' is approached.

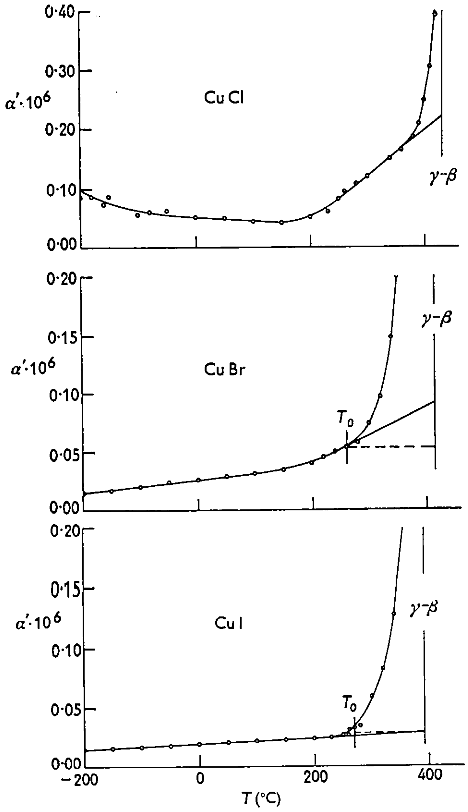

Fig. 4. 'Laval plots': α' as a function of T. Note the extrapolations above T_0 according to the 'Laval' (full line) and 'Merriam' (dashed line) procedures. The Lawson approximation (α = constant, $\alpha' = 0$) is equivalent to the abscissa.

The α' *versus* T plots shown in Fig. 4 conform only crudely to the predicted trends below T_0. Since α' is supposedly linear in temperature at 'high temperatures' empirical extrapolations may be made above T_0, as previously. However, several shortcomings render this procedure a tentative one: apart from the uncertainty in T_0 small errors in a–T expansion data are grossly magnified by the conversion to $d\alpha/dT$.

From Fig. 1 it will be appreciated that widely diverse estimates of 'normal' expansion result from different approaches. Procedure (iii) is the least dependent on error in experiment and data manipulation, although the 'Laval plots' suggest that this (and the other procedures) overestimates the 'anomalous' effect. That the 'Lawson extrapolation' (equivalent to the abscissa in Fig. 4) is a poor one is obvious from the standpoint of continuity.

The 'anomalous' expansion isolated for γ-CuBr and γ-CuI by the favoured method (iii) is best illustrated on $\ln (T^2 . \Delta\alpha)$ *versus* $1/T$ plots (Fig. 5), where $\Delta\alpha = \alpha(\text{observed}) - \alpha(\text{'normal'})$ and T is in °K. Consider the relationship

$$\Delta V/V = (n/N) . v = A \exp(-W/2kT) \qquad (1)$$

where ΔV is the 'anomalous' increase in crystal volume V due to the volume effect of thermal disorder, v and W are respectively the relative volume increment of an ion pair and energy associated with the formation of one point defect, k is Boltzmann's constant. It readily follows that

$$T^2 . \Delta\alpha = B \exp(-W/2kT) = (\tfrac{1}{3} . W/2k) . \Delta V/V \qquad (2)$$

where A, B are pre-exponential constants. The plots display curvature approaching the γ–β transition temperature. This may be due to either the presence of 'mixed' disorder or alternatively to the temperature dependence of W or B (Schmalzried, 1959). The latter possibility gains favour from the fact that the curvature of the ln (ionic conductivity) *versus* $1/T$ graphs (Jost, 1960) has been attributed to this effect (Lieser, 1956*b*).

Table 3 lists W and $\Delta V/V$ as derived from the linear portion of Fig. 5. (Similar analysis of the 'anomalous' expansions from (ii) shows that W is of the same order for γ-CuCl.) The values should be

Table 3. *W and $\Delta V/V$ (at γ–β transition) for γ-CuBr and γ-CuI*

	W (eV)	$(\Delta V/V).10^2$
γ-CuBr	3·1	0·3
γ-CuI	2·5	0·2

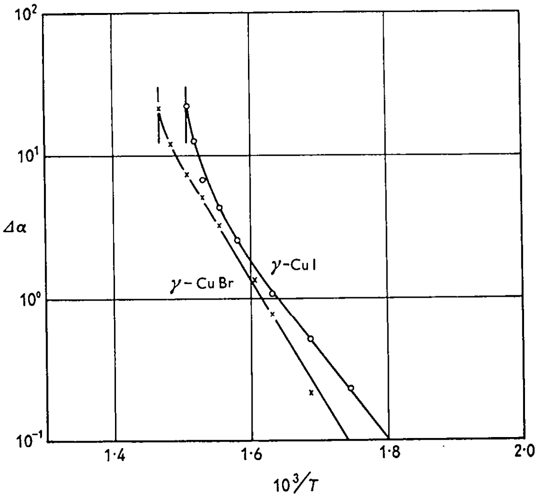

Fig. 5. Plot of ln ($T^2.\Delta\alpha$) *versus* $10^3/T$ for CuBr and CuI, for the 'Merriam procedure'.

compared with $W = 0{\cdot}7$ eV estimated for β-AgI from specific heat data (Lieser, 1954).

Frenkel defect models

One is now in a position to speculate on the actual nature of thermal disorder. It appears likely that the Schottky type plays only a minor role here. As a result of X-ray studies on β-AgI single crystals (Helmholz, 1935), α-AgI powders (Strock, 1935; Hoshino, 1957) and CuBr, CuI powders (Hoshino, Miyake & Takenaka, 1952; Hoshino, 1952; Hoshino & Miyake, 1958), various models of Frenkel disorder have evolved. These will now be considered in detail.

Silver iodide

(*a*) *β and γ modifications.* — A negative thermal expansion coefficient in β-AgI is thermodynamically in keeping with its other uniquely 'anomalous' properties, such as the positive pressure coefficient of ionic conductivity and the conversion to the NaCl-type structure under high pressure (Lieser, 1956*a*; Payne & Lawson, 1961). It is therefore only natural to attribute these anomalies to a common source, namely thermal defects.

Helmholz (1935) found his X-ray data on β-AgI consistent with an 'ideal' wurtzite ($B4$) structure at −180 °C but not at room temperature. This led him to postulate a disordered structure in which thermally activated Ag^+ ions occupy metastable sites as illustrated in Fig. 6(*a*). According to this model a positive 'anomalous' expansion may be expected: a cation approaching a 'Helmholz defect site' necessarily forces apart the three I^- ions comprising the closest tetrahedral face, resulting in a positive v_F. Such a model is contrary to a negative thermal expansion coefficient.

However, because of the small degree of disorder present at room temperature, Helmholz's conclusion is open to considerable doubt. This was in fact pointed out by Lieser (1956*c*, 1958) who suggested an alternative disorder structure in accord with the Helmholz data on β-AgI.* If thermal fluctuations become excessive, displaced Ag^+ ions may penetrate the 'energy hump' in any of the tetrahedral faces comprising the surrounding I^- ion lattice. Two types of interstice may then be occupied (Fig. 6(*b*)):

(I) A void with the same primary coordination (tetrahedral) as a normal lattice site.
(II) Octahedrally coordinated void (NaCl-type bonding).

There is one of each void available as a defect site per ion pair in the $B3$ and $B4$ lattices. Type (I) disorder, characterized by a structural energy similar to that of the normal lattice configuration, is not conducive to thermal activation — it is therefore readily accommodated in non-equilibrium quantities. However, type (II) may exist in thermal equilibrium to the extent of nearly 10% at 150 °C (Lieser, 1956*b*). Consideration of the Madelung potential about each defect centre indicates that types (I) and (II) are energetically favoured in the $B3$ and $B4$ structures respectively. Lieser (1956*a*, *c*, 1958) reconciles this conclusion with differences in several 'defect-sensitive' properties between β- and γ-AgI. The polymorphic behaviour of AgI may also be interpreted in terms of this model.

One now arrives at a possible mechanism for a negative dilatation. The radius of the interstitial

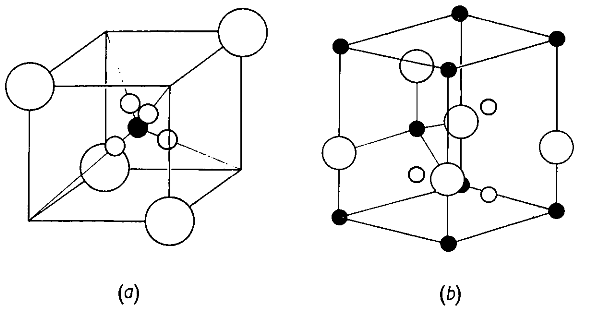

Fig. 6. Models of Frenkel disorder in $B3$ and $B4$ crystal lattices: (*a*) Helmholz model, showing metastable sites in a tetrahedrally bonded unit. (*b*) Lieser model, showing defect sites in the $B3$ lattice. Large circles represent anions, small black circles represent cations. Small open circles indicate defect sites.

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* Since the time of writing, further evidence (Burley, 1963) in this direction has appeared.

that a type (II) void may snugly accommodate is ~ 1·5 times that of the cation. The displacement of nearest neighbours toward the oppositely charged interstitial may prove sufficient to outweigh the outward relaxation about the vacated lattice site, thereby producing an overall contraction in one unit cell volume. If this is to counteract the 'normal' expansion the value of v_F (associated with a Frenkel defect) will require to be numerically greater than $-0{\cdot}01$ (as calculated from equation (1) on the basis that the 'normal' expansion is zero — even allowing for a typical positive expansion the magnitude of v_F does not appear excessive).

From Fig. 6(*b*) it is seen that the distance between two successive type (II) defect centres in the *B*4 lattice is $c/2=0{\cdot}82a$ along the *c* axis and *a* along the *a* axis. (In *B*3 they are necessarily equidistant in all axial directions.) With high defect concentrations one would expect a preferred contraction along the *a* axis of β-AgI, the repulsion between like Ag^+ ions being less in this direction. Although Fizeau's (1867) interferometric measurements show slight anisotropy the present data reveal no such trend. However, it is possible that an anisotropic effect may be obscured by experimental scatter.

γ-AgI has been described as a metastable disordered polytype of β-AgI produced by crushing the latter (Fridrichsons & Mathieson, 1962). (See Smith & Hill, 1956, for similar structural behaviour in ZnS.) The expansion trends (Fig. 7) are in conformity with the propagation of (type II) disorder in γ-AgI, although, as predicted by Lieser, to a somewhat less degree than in the β modification.

(*b*) *α modification.* — Strock proposed a structure for α-AgI consisting of a comparatively rigid body-centred-cubic I^- ion lattice throughout which the Ag^+ ions distribute themselves statistically among the Wyckoff 6(*b*), 12(*d*) and 24(*h*) equipoints of space group *Im*3*m*. This model is supported by the evidence of Hoshino. The 'molten' state of Ag^+ ions explains the prominent ionic transport properties inherent in α-AgI.

The structure is therefore one of nearly complete Frenkel disorder in the silver partial lattice between 150 °C and 555 °C with a very small amount ($<1\%$) of Schottky defects at higher temperatures. Disorder is reasonably independent of temperature and a somewhat regular expansion expected is indeed observed (Fig. 3).

Cuprous halides

(*a*) *γ modifications.* — The 'anomalous' expansion of the γ cuprous halides is shown to be associated with a defect mechanism characterized by a positive v_F in direct contrast to the negative value apparent in γ- and β-AgI. This favours Helmholz-type disorder in the copper partial lattice. Further evidence leaning toward this model in preference to that of Lieser is presented in the following:

(i) Hoshino, Miyake & Takenaka (1952) and Hoshino (1952) attempt to reconcile their X-ray intensity data with various models of Frenkel disorder in CuI and CuBr. The Helmholz model gives the best agreement with experiment.

(ii) Disorder becomes prevalent at much higher temperatures (above room temperature) in the cuprous halides as compared with AgI (−180 °C). Also, *W* is considerably greater in the former. These points suggest that the thermal vibrations of the Cu^+ ions in the cuprous salts are less vigorous than the Ag^+ ions in AgI and are therefore less likely to be excited into octahedral sites.

(iii) The radius ratio of cation and anion (as computed from Pauling ionic radii) increases in the order CuI, CuBr, CuCl, AgI, AgBr, AgCl. Since an increasing ratio is a measure of the tendency toward higher coordination, it follows that AgI is geometrically favoured over the cuprous halides to assume octahedral bonding. Mixed crystals of silver and cuprous halides do in fact reveal a tendency for the Cu^+ ion to occupy tetrahedrally bonded sites and Ag^+ ion octahedrally bonded sites. (For example, see Reinhold & Schulz, 1933, on the CuBr–AgBr system.)

(iv) Changes in properties such as specific volume (Fig. 7), entropy (Table 4), conductivity (Jost, 1960) are much less pronounced over the polymorphic transitions in the cuprous halides than in AgI. These are indicative of a less drastic structural rearrangement (as in Helmholz disorder) in the former.

(*b*) *β and α modifications.* — The γ–β transition is the 'reconstructive' polytypic *B*3–*B*4 transformation described by Buerger (1951). Since the two structures

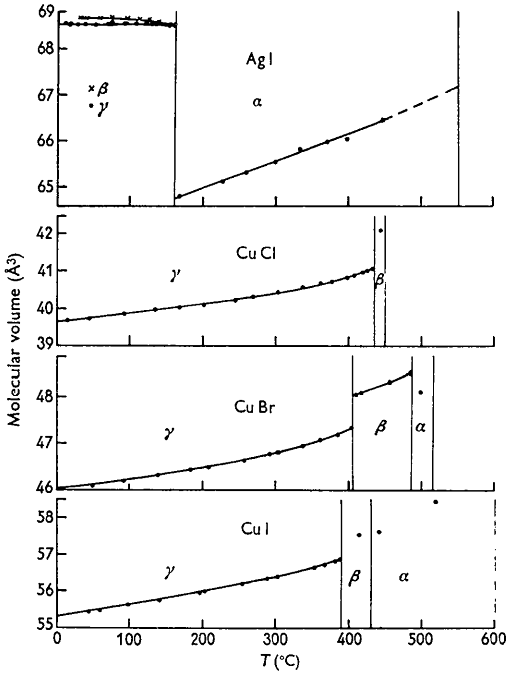

Fig. 7. Specific volume as a function of temperature.

Table 4. *Entropy changes for polymorphic transitions*

Substance	Transition	Entropy change (cal/mol.deg)	Reference
AgI	β–α	3·5	Lieser (1954)
		3·6	Hoshino (1957)
		4·8	Jost, Oel & Schniedermann (1958)
CuI	γ–(β–)α	3·8	Hoshino *et al.* (1952)
CuBr	γ–β	2·1	Hoshino (1952)
	β–α	0·9	

ideally have practically identical molecular volume and structure energy any increases in entropy and specific volume may be attributed to increases in Frenkel disorder. Treating the increase in specific volume (compare the 1–2% change with $\sim$0·3% 'anomalous' effect in the γ phases) as due entirely to the attaining of an 'averaged' Helmholz-type structure (*i.e.* $n/N \sim 100\%$) equation (1) yields a reasonable $v_F \sim$ 0·01–0·02.

Little is known about the α polymorphs. α-CuBr is believed to attain the same $B23$ structure as for AgI. However, although the change in specific volume over the β–α transition is negative for both substances, its magnitude is considerably less for the former. α-CuI reconverts to the $B3$ structure, but with 'averaged' Cu^+ ions. A transition between 'averaged' $B4$ and $B3$ structures would require little volume or entropy change. The limited data in the case of CuI does not permit one to establish the change in specific volume over the β–α transition precisely; however, at first sight it appears to be relatively small, as expected.

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