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Thermal Expansion of Silver Halides

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X-ray measurements of the thermal expansion of AgBr and AgCl in the temperature range −190 °C to the melting points are reported. The 'anomalous' rise in expansion below the melting points is consistent with the volume requirements of Frenkel defects with some 'mixed' disorder occurring at higher temperatures.

Introduction

The interest in the photographic properties and ionic transport mechanism in silver halides has aroused much speculation as to the nature of thermally activated defects in these crystals. Before about 1950 most of the evidence (Tubandt, 1932; Wagner & Beyer, 1936; Mott & Littleton, 1938; Mott & Gurney, 1940; Berry, 1951) favoured the Frenkel model but other workers (Mitchell, 1949; Teltow, 1949; Lawson, 1950; Kurnick, 1952; Ebert & Teltow, 1955; Fischmeister, 1956*a*, *b*; Zieten, 1956*a*, *b*) have since suggested the presence of some Schottky disorder, particularly at temperatures near the melting point. Because of the present state of experimental uncertainty and inadequate theoretical analysis the picture is still not clear.

Several attempts to use thermal expansion as a means of investigating the nature of point defects in crystals have been made since Lawson (1950) first analysed the silver bromide and silver chloride macroscopic data of Strelkow (1937). Lawson assumed that the 'normal' expansion coefficient of a defect-free lattice remained constant from room temperature to its melting point. His analysis of the 'anomalous' contribution appeared to be consistent with the volume requirements of the Schottky mechanism. Uno (1951) and Gertsriken (1954) employed a similar argument in examining some other substances. Berry (1951) measured some cell parameters of silver bromide at temperatures just below the melting point. Comparison of these measurements with Strelkow's led Berry to conclude that the disorder is predominantly Frenkel, with a permissible maximum of 0·2% Schottky defects. Zieten (1956*a*, *b*), using a dilatometer, remeasured the expansion of 'pure' and 'doped' AgCl and AgBr and supported the Schottky model for AgBr with the probability of mixed Frenkel–Schottky disorder at higher temperatures. The reverse mechanism was favoured for AgCl.

Prior to the work of Fischmeister (1956*a*, *b*) no serious attempt to establish a strict theoretical foundation for the isolation of the expansion of an undisturbed vibrating lattice had been made. Fischmeister considered the well known Gruneisen expansion equation derived on the basis of a slightly anharmonic vibrating crystal. His sophisticated treatment of the alkali halides seemingly explained their expansion without recourse to defects and also separated an 'anomalous' volume effect in the silver halide data of Strelkow. A comparison with Teltow's (1949) calculated defect concentrations from conductivity measurements implied a predominant Schottky process. However, although his analysis is theoretically sounder than those of the previous workers, it has since been criticized by Fletcher (1957), who demonstrated its insensitivity. In further, more rigorous, studies of high temperature expansion, Fletcher (1957, 1959, 1961) and Eastabrook (1957) have pointed out that a linear plot of the type obtained by Fischmeister may not necessarily substantiate the validity of his treatment. Additional evidence as to the inability of the Gruneisen theory to account for thermal expansion has been afforded by Mitra & Mitra (1957), who obtained grossly non-linear plots for some metals.

More recently, Merriam, Smoluchowski & Wiegand (1962) have stressed the significance of the 'knee' temperature observed in ionic conductivity and diffusion experiments. Below this temperature (T_0, say) thermally generated defects are present in quantities which are small compared with the concentration of impurity and other imperfections. At T_0, therefore, should be imposed a boundary condition that thermally activated defect concentrations are negligible, *i.e.* 'anomalous' volume contribution is effectively zero. Merriam *et al.*, in treating the expansion of rocksalt, selected the 'normal' expansion by considering a high temperature approximation of the Gruneisen equation. This indicates an expansion coefficient tending to a linear function in temperature for $T \gg \Theta$ (Θ = Debye temperature), in conformity with general experimental evidence. Despite the relatively low molar concentration of lattice defects in alkali halides at their melting points ($\sim 1 \times 10^{-4}$) the treatment revealed an 'anomalous' contribution to the expansion coefficient in the case of NaCl where the Fischmeister method was too insensitive.

Since the magnitude of defect molar concentrations in silver halides is $\sim 1 \times 10^{-2}$, *i.e.* ~ 100 times as great as in alkali halides, the accuracy requirements would be less stringent for a similar analysis. However, in view of large discrepancies in available expansion data for these compounds and the conflicting conclusions inferred from different treatments, much doubt must prevail over previous interpretations. To this end it was decided to obtain more comprehensive measurements of the expansion of the silver halides by an X-ray technique to supplement the meagre X-ray data avialable. A comparison with the macroscopic expansions of the other workers gives a measure of Schottky disorder and questions the reliability of Berry's earlier comparison. It is concluded that Frenkel disorder predominates in AgCl and AgBr with a small fraction of Schottky defects occurring near the melting point.

Experimental

Fine powders of each silver halide were prepared by precipitation from solutions of silver nitrate and excess potassium halide. A.R. grade materials were used in all cases. After many repeated washes the powders were vacuum-dried, crushed and vacuum-sealed in 0·5 mm silica glass capillary tubes for the high temperature camera and 0·3 mm Lindemann glass capillaries for use in the low temperature camera. The specimens were annealed below their respective melting points for several hours. A red safety light was used at all times when handling the materials. A spectroscopic analysis revealed a maximum total impurity content of $<0{\cdot}05\%$ in any one sample.

For measurement of lattice parameters from room temperature to the melting points a Unicam S.70 19 cm high-temperature camera was employed. A few modifications were necessary; the specimen support was improved and the furnace temperature controlled by an electronic device similar in design to that of Christy (1956). Temperatures could be controlled to within 1 °C at room temperature and 2–4 °C at 500 °C.

The platinum/platinum-13%-rhodium thermocouple installed to measure specimen temperature was calibrated according to the procedure described by Brand & Goldschmidt (1956). Some lattice parameters of silver were measured and compared with the macroscopic expansion data of Esser & Eusterbrock (1941). Balluffi & Simmons (1960) have recently shown that the X-ray and macroscopic expansions of silver are inseparable below 700 °C. The silver specimen was filed from spectroscopically pure silver rod and then enclosed in capillaries similar to those used for the other specimens. The random scatter of points on the calibration curve suggests that specimen temperature may be ascertained to within 1 °C at room temperature and 2 °C at 500 °C.

Some additional X-ray patterns were recorded at temperatures below room temperature on a 9 cm diameter camera designed by Cheesman and described by Hawes (1959). The overall film quality was much poorer than that acquired on the Unicam camera. A copper/constantan thermocouple, inserted in the specimen chamber, was calibrated by measuring silver unit cell lengths and comparing them with published data of Owen & Williams (1954). By this means specimen temperature could be ascertained to within 5 °C, the large variations reflecting the reduced accuracy of the smaller camera. Crushed ice, frozen CCl_4, dry ice and liquid air served as coolants surrounding the camera.

Unfiltered Ni K radiation was selected for all high-temperature photographs. Unfiltered radiation was preferable because of long exposures required ($\sim\frac{1}{2}$ day). Ni radiation gave superior back reflexion photographs for AgBr and AgCl, with lines at $\theta = 83$–$84°$ at room temperature. For the low-temperature equipment Cu K radiation (unfiltered) was the only target available.

Line positions on the film were measured on a sliding vernier scale. High quality lines could be reproduced to within $\pm 0{\cdot}02$ mm. On the 19 cm camera this represents an accuracy of 1 part in 30,000 for interplanar spacings with Bragg angle $\theta = 80°$.

Lattice parameters

Linear Nelson–Riley (1945) extrapolations were observed down to $\theta < 15°$ for each substance examined. At temperatures approaching the melting points, where many of the high-angle reflexions were considerably broadened or disappeared completely, this linearity was taken to imply that an extrapolation was still satisfactory, even if only lower angle lines were available. On this basis, all cubic cell dimensions were calculated according to a weighted least-squares procedure described by Hess (1951), but modified to accommodate the Nelson–Riley function. The rather lengthy computations were programmed for use on an IBM 1620 computer. A final correction (after Wilson, 1940) for the refraction of the X-rays, was applied.

The scatter of points on graphical extrapolations and repeated measurements of some films indicate a reproducibility of $\pm 0{\cdot}0001$ Å for AgCl and AgBr cell dimensions at room temperature. At higher temperatures, near the melting point, the precision reduces to $\pm 0{\cdot}001$ Å.

The mean lattice parameters of these halides at 25 °C, interpolated from lattice parameter/temperature graphs, agree to within 0·0001 Å with the accurate determinations published by Berry (1955).

Expansion results

Figs. 1 and 2 illustrate the temperature dependence of the AgCl and AgBr cell dimensions. Smoothed

results published by other workers are included for comparison, all being macroscopic data except those of Berry. The X-ray measurements of the author are seen to fall below the other curves. Eshelby (1954) and Balluffi & Simmons (1960) demonstrate theoretically that differences between macroscopic and X-ray expansion give a direct measure of Schottky disorder

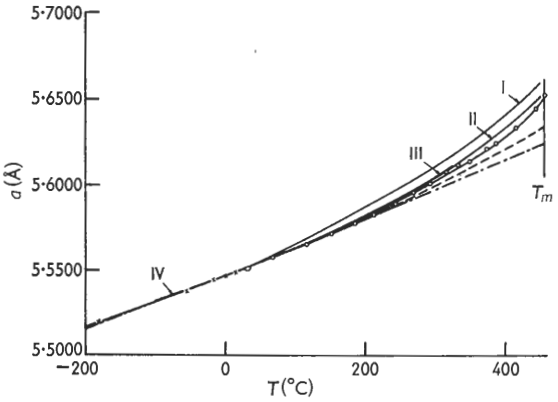

Fig. 1. AgCl: Lattice parameters against temperature:

Curve I:	Strelkow (1937), macroscopic.
Curve II:	Zieten (1956), macroscopic.
Curve III:	Sharma (1950), macroscopic.
Curve IV:	Sreedhar (1954), macroscopic.

—o—o—o—o— Author, X-rays (high-temperature camera).
—×—×—×— Author, X-rays (low-temperature camera).
·—·—·—·— Theoretical Gruneisen curve in defect-free lattice.
– – – – – – Theoretical 'normal' curve assuming linear expansion coefficient above 'knee' temperature.

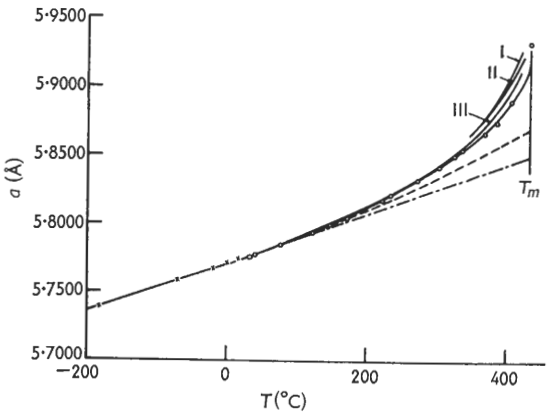

Fig. 2. AgBr: Lattice parameters against temperature:

Curve I:	Strelkow (1937), macroscopic.
Curve II:	Berry (1951), X-rays.
Curve III:	Zieten (1956), macroscopic.

—o—o—o—o— Author, X-rays (high-temperature camera).
–×–×–×– Author, X-rays (low-temperature camera).
·—·—·—·— Theoretical Gruneisen curve in defect-free lattice.
– – – – – – – Theoretical 'normal' curve assuming linear expansion coefficient above 'knee' temperature.

in the ionic crystals. The differences between the author's and the other curves may be attributed to either systematic temperature measurement errors, an effect due to specimen history or purity (Berry, 1955), or the phenomenon expected from Schottky disorder.

The maximum separation (δa) between extreme macroscopic (Strelkow) and X-ray (author) curves (Figs. 1 and 2) is found to be 0·026 Å for AgBr and 0·013 Å for AgCl, just below their melting points (T_m). This corresponds to an upper limit of Schottky defect molar concentrations of 1·3% and 0·7% respectively, in accordance with the relationship:

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

However, on the basis of a thermodynamical consistency test, Lawson (1957) has found Zieten's AgBr expansion results to be more compatible with existing specific heat and compressibility data than those of Strelkow. The former's results also exhibit smaller spread. Moreover, Sharma (1950) and Zieten show good agreement with the expansion of AgCl (Fig. 1). The maximum separations between the more accurate expansions of Zieten and those of the author suggest $(n/N)_s \simeq 0{\cdot}5\%$ (AgBr) and $\simeq 0{\cdot}3\%$ (AgCl).

Furthermore, one would expect macroscopic and X-ray expansions to be inseparable at the 'knee' temperature. According to the ionic conductivity studies of Shapiro & Kolthoff (1947), who examined variously treated precipitates of AgBr, T_0 is 97 °C for an annealed sample. Since this specimen had a similar history to those used in the above expansion measurements, and on the assumption that the degree of purity was of the same order, 97 °C was adopted as the 'knee' temperature for AgBr. Similar studies are not known for AgCl. The conductivity and diffusion data of Compton & Maurer (1956) were consulted, yielding $T_0 \simeq 143$ °C.

At T_0, for both substances, Zieten's macroscopic and the author's X-ray curves in Figs. 1 and 2 differ by 0·002 Å. It would appear likely that this small effect is a contribution from either of the two alternatives to the Schottky effect, offered above. An explanation in terms of specimen impurity is unlikely because more than one sample, from different batches, was employed to compile the expansion data. Subtracting this effect as a crude (but small) correction factor from the measured Zieten/author separation, one arrives at more probable concentrations of 0·4% (AgBr) and 0·2% (AgCl).

Isolation of the 'anomalous' expansion

To examine the extent of the volume effect of lattice disorder the technique of Fischmeister was tentatively adopted. Consider the inverted Gruneisen equation:

$$V_0/\Delta = Q_0/E - p$$

where

$\Delta = V_T - V_0$

V_T, V_0 = unit cell volumes at temperatures T °K, 0 °K

E = Debye energy function

$$= 2.(9RT).(\Theta/T)^3 \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1}$$

(factor 2 for binary compounds)

$Q_0 = V_m/\gamma\varkappa_0$

V_m = molar volume (at 0 °K)

γ = Gruneisen constant

$\varkappa_0$ = compressibility (at 0 °K)

p = constant, depending on the interatomic potential function.

Fischmeister treated Q_0 and p as empirical constants, attaching little significance to their theoretical aspect.

Graphs of V_0/Δ *versus* $1/E$ clearly illustrate the contribution of thermally generated defects to the lattice parameters near the melting points. However at lower temperatures, in the region $T \sim \Theta$, the curves rapidly depart from linearity, a trend independent of a wide range of chosen Θ. In the high temperature region, where the plots are least sensitive to deviations from the Gruneisen Law, a reasonable estimate of the 'normal' curve was still possible.

Table 1 gives Q_0 and p. It was noticeable that small variations in these parameters greatly influenced values of the 'anomalous' expansion so determined. The Gruneisen curves corresponding to these parameters are illustrated as dot-dashed lines in Figs. 1 and 2.

Table 1. *Results from Gruneisen plots*

	$Q_0 . 10^3$	p	W (eV)	A	$(\delta V/V) . 10^2$ (at T_m)
AgCl	143·0	1·9	0·756	5·178	1·31
AgBr	137·6	1·6	0·529	1·791	2·34

From the following equation, readily derived from statistical mechanics:

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

where

δV = 'anomalous' increase in lattice volume V due to the volume effect of lattice defects

n/N = molar concentration of lattice defects

v = relative volume increment of an ion pair associated with formation of one point defect

A = pre-exponential constant

W = energy required to form one lattice defect (eV)

k = Boltzmann's constant

a plot of $\ln(\delta V/V)$ *versus* $1/T$ yields W. The value of W is not critically dependent on Q_0 and p when $W < 1$ eV. These semi-logarithmic plots were linear to just below the melting points, where a slight increase in $\ln(\delta V/V)$ occurred.

Much of the uncertainty occurring in Fischmeister's treatment must be ascribed to the relatively small effect of point defects on lattice parameters. More sensitive to small disturbances is the linear expansion coefficient (α). Although much experimental precision is sacrificed by expressing the data in terms of this quantity its relative increase is calculated to be ~ 100 times as great as the corresponding change in cell parameter when defects dilate the lattice. The choice of the 'normal' expression is therefore far less critical when expansion coefficients are considered. Any errors introduced in determining 'anomalous' expansions tend to reflect experimental discrepancies rather than theoretical deficiencies.

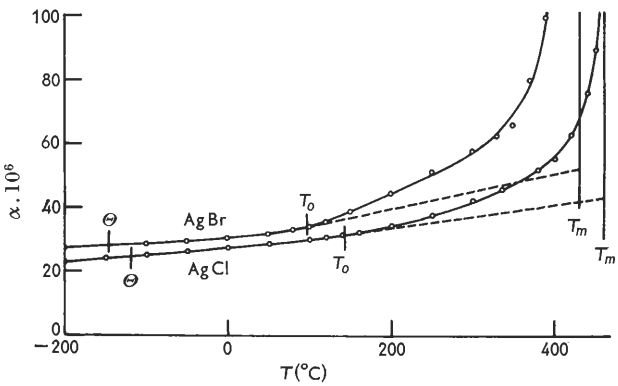

Fig. 3. Thermal expansion of AgBr and AgCl against temperature. Dashed line shows assumed linear expansion of defect-free lattice above 'knee' temperature.

Fig. 3 shows the calculated expansion coefficients of AgBr and AgCl. Also included in the diagram are 'normal' lattice vibration expansion curves, assumed linear above T_0 ($T_0 > 2\Theta$ here), a region where the Debye energy E is found to increase at an approximately constant rate with temperature. They are shown in Figs. 1 and 2 as dashed lines.

To calculate the energy of formation of a point defect from the anomalous expansion coefficient, equation (1) is differentiated with respect to temperature:

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

where $\delta\alpha$ = anomalous expansion coefficient. A graph of $\ln(T^2 . \delta\alpha)$ *versus* $1/T$ should give a straight line of slope $(-W/2kT)$. The curves observed however (Fig. 4), which are characterized by a departure from linearity above a 'kink' temperature (T_1, say), could be more suitably expressed in the form:

$$T^2 . \delta\alpha = B_1 \exp(-W_1/2kT) + B_2 \exp(-W_2/2kT)$$

indicating the possibility of two activation processes. Alternatively, the same phenomenon may be due to temperature dependence of v (occurring in pre-exponential B) and W, without recourse to a second activation process (Schmalzried, 1959).

Table 2. *Results of* $\ln(T^2 . \delta\alpha)$ *versus* $1/T$ *plots*

	W_1	$B_1 . 10^{-4}$	W_2	$B_2 . 10^{-18}$	$(\delta V/V) . 10^2$ (Line I) (at T_m)	$(\delta V/V) . 10^2$ (Line II) (at T_m)
AgCl	0·939 eV	2·032	5·09 eV	7·844	0·66	0·25
AgBr	0·590	0·168	4·51	1·854	1·18	1·90

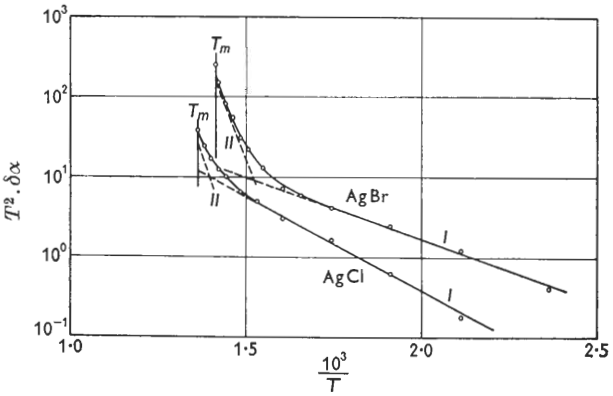

Fig. 4. Plot of $\ln(T^2 . \delta\alpha)$ against $10^3/T$ for AgBr and AgCl.

Consideration of defect models

Take firstly the assumption of the double activation process, with constant formation energies and pre-exponential factors. Table 2 gives the parameters W and B corresponding to each process. Similar 'kinks' to those encountered in Fig. 4 (at ~ 315 °C for AgBr and ~ 370 °C for AgCl) have been observed in the same temperature regions by others (Teltow, 1949; Kurnick, 1952; Kobayashi, 1952; Kanzaki, 1954; Ebert & Teltow, 1955; Zieten, 1956*a*, *b*) from measurements of heat capacity, conductivity and thermal expansion.

The straight lines labelled I in Fig. 4 are taken to be associated with a single defect process. Consider the Schottky mechanism for which v_s is believed to be $\simeq 1·5$ (Mott & Littleton, 1938; Kurnick, 1952; Zieten, 1956*a*, *b*). Whereas the defect volume contribution as derived from macroscopic measurements is proportional to v_s the same quantity as obtained from X-rays is proportional to $(v_s - 1)$ since lattice dimensions are unaffected by the vacancies created on forming Schottky sites. Therefore, even if v_s is numerically as large as 2 the separation between macroscopic and X-ray expansion curves will exceed or at least equal that between the X-ray and 'normal' expansions. On the other hand X-ray and macroscopic measurements will be identical where only Frenkel disorder prevails, regardless of the value of v_F.

Inspection of Figs. 1 and 2 reveals that the condition for Schottky disorder is not fulfilled below T_1, except in AgCl when Strelkow's curve is considered. Since Zieten's data warrant greater weight the Schottky model is considered highly improbable. This leaves Frenkel disorder. Although the X-ray measurements do not coincide exactly with those of Zieten the Frenkel requirement is far more closely satisfied. Furthermore, at T_0 where the concentration of thermal defects should be negligible, the separation is of the same order as at T_1. Therefore, allowing for a small systematic error Zieten's and the author's results agree within experimental scatter.

Table 3. *Lattice defect energy of formation* (W) *and molar concentration* (n/N) *at the melting points* (*various sources*)

Source	AgCl W	AgCl $(n/N) . 10^2$	AgBr W	AgBr $(n/N) . 10^2$
Ionic conductivity and diffusion				
Koch & Wagner (1937)	1·08 eV	0·64	0·876 eV	2·0
Shapiro & Kolthoff (1947)			0·841	
Teltow (1949)			1·27	1·3
Ebert & Teltow (1955)	1·56	0·35		
Kurnick (1952) (Frenkel)			1·19	0·77
Kurnick (1952) (Schottky)			1·47	3·1
Specific heat				
Christy & Lawson (1951)			1·28	3·7
Kanzaki (1951) (Frenkel)			1·17	0·25
Kanzaki (1954) (Schottky)			1·70	1·5
Kobayashi (1952)	1·53	0·75		
Thermal expansion				
Lawson (1950) (on Strelkow's data as corr. by Fischmeister)	0·62		1·08	
Fischmeister (1956)	0·976		1·59	
Zieten (1956) (Frenkel)	1·13		2·52	
Zieten (1956) (Schottky)			0·894	

Assuming Frenkel disorder is the prominent mechanism below T_1, one can calculate v_F from equation (1), using $\delta V/V$ from Table 2 and n/N from conductivity and specific heat experiments (Table 3). However, in view of the diversity of available data little weight can be attached to such calculations, which Lawson and Fischmeister employed to identify Schottky disorder in AgBr.

At temperatures above T_1 the Zieten/author expansions exhibit their greatest differences. This is in accordance with the proposal of an additional Schottky disorder in the higher temperature region, thus explaining the rise in the $\ln(T^2.\delta\alpha)$ *versus* $1/T$ graph. A quantitative discussion is not considered warranted in this case because of extreme sensitivity of the parameters to small errors in the analysis.

The second means of explaining the non-linearity of the 'anomalous' contribution *versus* $1/T$ graphs is due, according to Schmalzried, to the variation of W and v. By this treatment an explanation is possible in terms of Frenkel disorder only. However, the presence of a small percentage of Schottky defects at very high temperatures would appear to contribute at least partially to this high temperature effect.

Discussion

Tables 1 and 2 permit a comparison of experimental results with those listed in Table 3. W_1 is found to be slightly higher than the corresponding W derived by the Fischmeister procedure, giving rather better agreement with other workers. Moreover, the increased sensitivity of the second treatment accentuates the high temperature disorder contribution. The 'normal' expansion derived is not so dependent on accuracy requirements, and is therefore accorded more weight.

The quantity W_2 obtained is not discussed quantitatively, since it is strongly influenced by small inaccuracies. Furthermore, if sufficiently large quantities of two defect types co-exist, mutual interaction is certain to have a profound effect on the equilibrium concentrations of each. It may not be valid to treat lines II (Fig. 4) as a measure of the second type of point defect since it no longer necessarily holds that lines I can be extrapolated above T_1. As Zieten has pointed out, large defect concentrations at the higher temperatures may also modify the fundamental lattice expansion in this region, giving rise to a false appraisal of the 'anomalous' volume contribution near the melting point. Again, the constants W and v are likely to become more variable as the defect concentrations and temperature fluctuations increase near the melting point.

A similar argument holds regarding the accuracy of pre-exponential constants A and B_1, B_2. Whereas A and B_1 yield values in accordance with Mott & Gurney's estimation for Frenkel defects, the B_2 for AgCl and AgBr are far in excess of the somewhat larger figure ($\sim 10^8$) predicted for Schottky disorder. This fact is attributed to the extreme sensitivity of B_2 to small inaccuracies incurred during experimental procedure and subsequent mathematical analysis of results and especially to the inadequacy of the theory above T_1, as outlined above. Little or no significance should therefore be attached to the B_2 so derived until the behaviour of the lattice above T_1 is more clearly understood.

The view expressed by Lawson, Fischmeister and Zieten, that the expansion of AgBr is compatible with Schottky disorder below T_1, cannot be completely repudiated here, although the comparison of X-ray and macroscopic data does not favour this proposal. The rather poor agreements between the macroscopic expansion of Strelkow and Zieten, and the X-ray expansions of Berry and the author, do not allow for any definite conclusions although Frenkel disorder is more likely to be the dominant mechanism. Studies on the silver halides similar to those carried out on metals by Simmons & Balluffi (1960*a*, *b*; 1962), where macroscopic and X-ray expansions are measured on the same materials and all possible precautions are ensured to subject the specimens to identical treatment, would be more conclusive. Once the Schottky fraction is established an understanding of the defect expansion contribution will be greatly simplified.

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