

Matematisk-fysiske Meddelelser  
udgivet af  
Det Kongelige Danske Videnskabernes Selskab  
Bind **32**, nr. 2

---

Mat. Fys. Medd. Dan. Vid. Selsk. **32**, no. 2 (1959)

---

THE STRUCTURE  
OF PEROVSKITE-LIKE CÆSIUM  
PLUMBO TRIHALIDES

BY

CHRISTIAN KN. MØLLER



København 1959  
i kommission hos Ejnar Munksgaard

## Synopsis

Crystalline compounds of composition  $\text{CsPbX}_3$ , where  $X = \text{Cl}$  or  $\text{Br}$ , may be prepared either from aqueous solutions or by fusing  $\text{CsX}$  and  $\text{PbX}_2$ . The pale yellow  $\text{CsPbCl}_3$  has cubic perovskite structure above  $47^\circ\text{C}$ . ( $a = 5.605 \text{ \AA}$ ), the orange-coloured  $\text{CsPbBr}_3$  above  $130^\circ\text{C}$ . ( $a = 5.874 \text{ \AA}$ ). Below these temperatures the structures are slightly distorted, but apparently without changes of volume at the transition points.  $\text{CsPbBr}_3$  below  $130^\circ\text{C}$ . (and possibly also  $\text{CsPbCl}_3$  below  $47^\circ\text{C}$ .) exhibits a superstructure, but not above this temperature. Application of Fourier methods shows that above as well as below the transition points, both the halogen atoms and the Cs-atoms are a little displaced from those positions expected for an ideal perovskite structure. Structure factors have been calculated on the assumption that each halogen atom occupies one of four, each Cs-atom one of six close-lying potential-minima at random; they show excellent agreement with the observed structure factors. It is suggested that such a delocalization of certain atoms may be a common feature in cubic perovskite structures where the tolerance factor  $t \neq 1$ . The  $\text{PbCl}$ -distances are  $2.86 \text{ \AA}$  and the  $\text{PbBr}$ -distances  $2.99 \text{ \AA}$ , i.e. considerably shorter than the sum of the corresponding ionic radii.

## Introduction

It has been demonstrated in a previous paper<sup>1</sup> that  $\text{CsPbI}_3$  can exist in a black perovskite-like modification besides the yellow, orthorhombic form stable under ordinary conditions. It will be shown in the present study that  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$  also form perovskite-like structures which in this case are the stable modifications.  $\text{CsPbF}_3$  has already been found by O. SCHMITZ-DUMONT and G. BERGERHOFF to belong to this structure type<sup>2</sup> with the unit cell edge  $a = 4.80 kX$ .

Ideally, crystals with perovskite structure are cubic with one molecule in the unit cell,<sup>3</sup> but very often small deviations from cubic symmetry are found. However, in such cases there usually is a transition temperature above which the structure is strictly cubic.<sup>4</sup> With only one molecule  $\text{ABX}_3$  in a cubic unit cell one would expect that all the atomic positions were fixed by symmetry. This argument has been widely used, but may not always be applicable for the following reasons. It is known that alloys exist which exhibit a cubic structure, but where the cubic symmetry is of a statistical nature so that the distribution of atoms within only one unit cell at definite lattice sites need not at all conform to the observed "average symmetry".<sup>5</sup>

Secondly, it is generally agreed that crystals with perovskite structure belong to the so-called defect structures,<sup>3</sup> and as far as the author is aware, the nature of the defects in this case is not yet understood.

If we imagine the ions to be solid spheres with definite ionic radii  $r_A$ ,  $r_B$ , and  $r_X$  the following relation can easily be demonstrated for the ideal perovskite structure:

<sup>1</sup> C. K. MØLLER, The Structure of  $\text{CsPbI}_3$ , Mat. Fys. Medd. Dan. Vid. Selsk. **32**, No. 1 (1959).

<sup>2</sup> O. SCHMITZ-DUMONT und GÜNTHER BERGERHOFF, Z. anorg. u. allgem. Chem. **283**, 314—329 (1956).

<sup>3</sup> See e.g. (a). R. C. EVANS, Crystal Chemistry p. 204—214, Cambridge 1939. (b) A. F. WELLS, Structural Inorganic Chemistry p. 112, p. 330, Oxford 1945.

<sup>4</sup> H. D. MEGAW, Ferroelectricity in crystals, Chapters 4 and 5. Methuen, London 1957.

<sup>5</sup> See e.g. Ref. 3a p. 109.

$$\frac{r_A + r_X}{r_B + r_X} = \sqrt{2} \cdot t, \quad (1)$$

where  $t = 1$ . However, for many crystals with perovskite structure  $t$  will be found to be different from 1 — usually in the range  $0.8 < t < 1$  when we insert the generally accepted ionic radii.<sup>1</sup>

We can interpret this either as an observable effect of the defect nature of these crystals, or as an indication that the ions are not solid spheres with fixed ionic radii. In fact, it has been proposed to use special ionic radii for ions when they form crystals of this type,<sup>2</sup> but from the observations to be described in what follows this procedure does not seem to be recommendable. It is presumably true that the bonding between the atoms in perovskite structures is mainly ionic and may be modified by polarization so that the interatomic distances will be shorter than calculated from the ordinary ionic radii, but this can scarcely justify the use of separate "perovskite ionic radii".

In order to clarify some of the problems connected with the perovskite structure a detailed investigation has been made of  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$ , as will now be described.

### Preparation and general properties

As has been shown by H. L. WELLS<sup>3</sup> and coworkers crystals with the compositions  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$  can be prepared by dissolving  $\text{PbCl}_2$ , resp.  $\text{PbBr}_2$ , in a hot aqueous solution of  $\text{CsCl}$ , resp.  $\text{CsBr}$ , of suitable concentration and then left to cooling. Besides this method of preparation we have found that compounds of the type  $\text{CsPbX}_3$ , where  $X = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$  can also be obtained by fusing  $\text{CsX}$  and  $\text{PbX}_2$  in the correct stoichiometric proportion. The identity of the crystalline compounds prepared by either method was proved by the identity of their X-ray powder diagrams and transition temperatures (see below).

The crystals grown in solution are quadratic or rectangular in shape, those of  $\text{CsPbCl}_3$  pale yellow and those of  $\text{CsPbBr}_3$  orange coloured. Their refractive indices are high, above 1.74.

Although the crystals are decomposed by water it was possible to determine the density of  $\text{CsPbCl}_3$ -crystals by the flotation method in a Clerici's

<sup>1</sup> V. M. GOLDSCHMIDT, Z. tech. Phys. 8, 256 (1927).

<sup>2</sup> S. GELLER, Acta Cryst. 10, 248 (1957).

<sup>3</sup> H. L. WELLS, Z. anorg. Chem. 3, 195 (1893).

solution<sup>1</sup> of known density:  $d = 4.21 \text{ g/cm}^3$ . With a rather coarse powder of  $\text{CsPbCl}_3$  a pycnometer method gave  $d = 4.24 \text{ g/cm}^3$  in reasonable agreement with the first result.

### Examination with the polarizing microscope, transition temperatures

Under the polarizing microscope the coloured crystals of  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$  appear birefringent and both show parallel extinction. By use of the quartz-wedge strong evidence was found from observation on a single crystal of  $\text{CsPbCl}_3$ , where the directions and the lengths of the axes had been determined by X-ray methods, that this crystal was (uniaxial) positive. Between crossed nicols very often thin twin lamellae can be observed, which form angles of  $45^\circ$  with the external edges. Twin formation with (110) as composition plane can easily be observed on thin crystals which between crossed nicols show first order grey as interference colour: On insertion of the gypsum plate (parallel to the extinction direction) one side of the composition plane gives yellow, the other side blue as the resulting interference colour. When these crystals of  $\text{CsPbCl}_3$  or  $\text{CsPbBr}_3$  are heated under the polarizing microscope with crossed nicols, the interference colours change continually, first slowly and then faster and faster, till they finally disappear at  $46.9^\circ\text{C}$ . or  $130^\circ\text{C}$ ., respectively. This shows that the crystals become optically isotropic above these temperatures and attain cubic symmetry. Qualitatively one gets an impression that the interference colours, which for the same crystal is a measure of its birefringence, depend on the temperature in much the same way as the axial ratio in fig. 1. On cooling, the interference colours reappear at the same temperatures, so that the changes are completely reversible. (Temperature calibration was made by determining the known melting points for substances such as urea, benzoic acid, etc.).

### X-ray investigations. Unit cell dimensions

Powder diagrams of  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$  have been obtained in a Guinier type focussing camera with  $\text{CuK}_\alpha$ -radiation. Whenever accurate  $\sin^2\theta$ -values had to be determined, the powders were mixed with NaCl (Kahlbaum, geschmolzen) which served as a standard calibration substance—due regard been paid to the dependence of its lattice constant on the temperature.<sup>2</sup>

<sup>1</sup> H. E. VASSAR, *Am. Mineral.* **10**, 123 (1925).

<sup>2</sup> H. v. BERGEN, *Ann. Phys.* **39**, 553—72 (1941).

In order to obtain diagrams of the powders at elevated temperatures the sample was fixed with the smallest possible amount of Canada balsam on a thin cover glass. This was squeezed into position between the circular metal holder and a piece of perforated mica with 6–7 turns of a 0.2 mm thick Ni-Cr-wire which could be electrically heated. It was found that the hot wire did not seriously affect the X-ray diagrams when it was kept perpendicular to the cylinder axis of the curved quartz-monochromator, and hence the samples were kept stationary, not rotated as is usual during the exposures. The temperatures were estimated from measurements of the resistance of the hot wire during operation, the transition temperatures determined by the optical investigation above being used as fix points.

Indices could be assigned to the "reflections" on the powder diagrams by application of the general formula

$$\sin^2 \vartheta = \frac{\lambda^2}{4} \left\{ \frac{1}{a^2 \sin^2 \gamma} h^2 + \frac{1}{b^2 \sin^2 \gamma} k^2 + \frac{1}{c^2} l^2 - \frac{2 \cos \gamma}{ab \sin^2 \gamma} hk \right\}, \quad (2)$$

where in our case  $\gamma$  was either  $90^\circ$  or very close to  $90^\circ$  and  $a = b \simeq c$ . The lattice constants for the crystals at different temperatures were finally evaluated from the coefficients to  $h^2$ ,  $l^2$  and  $hk$  in (2) giving best agreement between observed and calculated  $\sin^2 \vartheta$ -values. They are reproduced together with indices, estimated intensities, and  $\sin^2 \vartheta$ -values in Tables 1 and 2 ( $\lambda$  (CuK $\alpha$ ) = 1.5418 Å).

A few diffuse lines on the Guinier-diagrams of CsPbBr $_3$  below the transition temperature (130°C.) cannot be accounted for with the indexing in Table 2 unless the unit cell axes are doubled. However, in order to maintain the connection with the cubic unit cell, instead of doubling the axes we have chosen to use fractional indices for these reflections. It is characteristic of these lines that they decrease in intensity as the crystalline powder is heated above room temperature, and practically disappear when the unit cell axes become of equal length at 130°C., only very faint diffuse bands being left in their place on the diagrams taken of the cubic form. From this behaviour one would infer that the lines mentioned are due to a superstructure which "melts" in the crystal at 130°C., only leaving some degree of "local order" reminiscent of the superstructure.

Also CsPbCl $_3$  in the tetragonal form shows a few lines of this type, but it is difficult to decide whether they really disappear at 47°C., and besides there are some rather sharp, very weak lines as well, which completely persist above 47°C. However, it has turned out that the latter originate from



TABLE 2. Comparison of observed and calculated

Indices <i>h k l</i>	Room temperature			Temp. about 120°C.		
	Intensity estimated	$10^4 \cdot$ $\sin^2 \vartheta_{\text{obs.}}$	$10^4 \cdot$ $\sin^2 \vartheta_{\text{calc.}}$	Intensity estimated	$10^4 \cdot$ $\sin^2 \vartheta_{\text{obs.}}$	$10^4 \cdot$ $\sin^2 \vartheta_{\text{calc.}}$
001	m	0172	0172	m	0172	0171
100	(m)-s	0175	0175	m	0173	0173
011	} vs	0347	0347	} s	0345	0344
110						
110	w	0352	0352	} vw	0433	0433
$\frac{1}{2} \frac{3}{2} 0$	w	0437	0436			
$\frac{1}{2} \frac{3}{2} \frac{1}{2}$	} vw	0474	0476. <sub>5</sub>	} —	—	—
$(\frac{1}{2} \frac{3}{2} \frac{1}{2})$						
111	w	0520	0520	} w	0518	0517
111	vw	0524	0524			
$\frac{1}{2} \frac{3}{2} 1$	w	0610	0609	vw	0604	0604
002	(m)-s	0687	0687	m	0683	0684
200	s	0700	0700	m-s	0693	0693
012	w	0862	0862	vw	0857	0857
021	} m-w	0871	0869	} w	0864	0864
120						
120	vw	0880	0879	} w	1029	1030
112	m	1038	1039			
211	m	1043	1043	} w-m	1038	1037
211	m	1053	1051			
022	m-s	1386	1387	m	1377	1377
220	vw?	1409	1408	vw	1385	1386
212	vw	1565	1566	(v)w	1550	1550
130	vw	1744	1744	vw	1731	1732
013	vw	1721	1721	—	—	—
222	—	—	—	vw	2068	2070
123	—	—	—	—	—	—
Unit cell.	$a = b = 5.827 \text{ \AA} \quad c = 5.891 \text{ \AA}$ $\alpha = \beta = 90^\circ \quad \gamma = 89^\circ 65'$ Volume: 200.0 $\text{\AA}^3$			$a = b = 5.859 \text{ \AA} \quad c = 5.895 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$ Volume: 202.3 $\text{\AA}^3$		

cell dimensions it may be concluded that  $\text{CsPbBr}_3$  also has only one molecule in the cubic unit cell. Perovskite structure is then very likely for these compounds, but, as will be shown below, intensities calculated on the basis of the atomic parameters required by the appropriate symmetry only in a rough qualitative way agree with the observed ones. The "tolerance factor"  $t$  from equation (1) is about 0.8.

### Temperature dependence of the axes

Powder diagrams of  $\text{CsPbBr}_3$  taken at four different temperatures have been indexed and the results together with the lattice constants deduced from them are reproduced in Table 2. It is seen that as the crystals are cooled

$\theta$ -values for CsPbBr<sub>3</sub> at different temperatures.

Temp. about 125° C.			Temp. about 135° C.			Indices <i>h k l</i>
Intensity estimated	10 <sup>4</sup> · sin <sup>2</sup> $\theta_{obs}$ .	10 <sup>4</sup> · sin <sup>2</sup> $\theta_{calc}$ .	Intensity estimated	10 <sup>4</sup> · sin <sup>2</sup> $\theta_{obs}$ .	10 <sup>4</sup> · sin <sup>2</sup> $\theta_{calc}$ .	
m-s	0172	0172	m	0172	0172	001
s	0344	{ 0345 0346 }	s	0345	0344	100 011 110 110 110
—	—	—				$\frac{1}{2}$ $\frac{3}{2}$ 0
—	—	—				$\frac{1}{2}$ $\frac{3}{2}$ $\frac{1}{2}$
—	—	—				( $\frac{1}{2}$ $\frac{3}{2}$ $\frac{1}{2}$ )
m-w	0516	0517	w	0516	0516	111 111
—	—	—				$\frac{1}{2}$ $\frac{3}{2}$ 1
m	0688	0687	s	0689	0689	002
m-s	0692	0691				200
(v)w	0861	0860				012
w	0865	0864	m	0862	0861	021 120 120
m-s	1036	{ (1033) 1036 }	m-s	1035	1035	112 211 211
m-s	1379	{ 1378 1382 }	m-s	1379	1378	022 220
vw	1551	1551	w-m	1546	1550	212
vw	1725	1728	vw	1721	1722	130
—	—	—	vw	2065	2066	013
vw	2069	2067	vw	2411	2411	222
vw	c. 2400	2408	vw	2411	2411	123
$a = b = 5.864 \text{ \AA}$ $c = 5.881 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$ Volume: 202.2 Å <sup>3</sup>			$a = b = c = 5.874 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$ Volume: 202.7 Å <sup>3</sup>			Unit cell.

from temperatures above 130°C. the unit cell changes from cubic through tetragonal to monoclinic symmetry at room temperature. Although the changes of the axes are easily demonstrated, the change of volume of the (pseudo-)unit cell when the transition point at 130°C. is passed, presumably is not significant.

Instead of making a similar investigation on powders of CsPbCl<sub>3</sub> at several different temperatures, which would be rather time-consuming, it was chosen to measure the changes of the axes of a single crystal. The crystal was carefully adjusted on a Weissenberg goniometer and a series of 3° oscillation photographs were taken of the reflections 071 and 017, which have  $2\theta = 155^\circ$  for CuK <sub>$\alpha$</sub> -radiation. The layer-line screen was used to separate the zeroth layer line, and the film cylinder (diameter 57.3 mm) was kept

stationary for each pair of exposures: 071 at the "top" and the "bottom" of the film. Then the film cylinder was displaced 3.0 mm (the width of the slot in the layer-line screen) and the oscillation regions of the crystal changed so that now two similar exposures could be taken of 017 at the same temperature. After that the temperature was changed, the film cylinder displaced 3.0 mm, and a set of four exposures taken at the new temperature, and so on. Exposure times were about 10 minutes.

The crystal could be heated by a controlled stream of  $N_2$  from a cylinder, passing a flowmeter and a very small, electrically heated "oven", which was placed immediately in front of the crystal. Temperature control was afforded by a copper-constantan thermocouple in connection with a millivoltmeter. The oven-current could be read on an ammeter. Calibration was made in the following way. Two small polaroids were placed on either side of the crystal, "crossed", but with maximum light passing through the crystal when it was illuminated with a beam of light through the pin-hole system of the goniometer, and the crystal was watched through the microscope attached to the goniometer. With constant  $N_2$ -flow the oven-current was slowly increased till the crystal just became dark (optically isotropic). The temperature must then be  $47^\circ C$ . For the same rate of flow of  $N_2$  and nearly constant room temperature it was then assumed that there was linear dependence between the thermoelectric power of the thermocouple and the temperature of the crystal for not too wide a range of temperatures.

The relation between the changes in glancing angles  $\vartheta$  measured on the film and the changes in axial lengths is obtained from (2) by differentiation. For 071 and 017 and with  $\Delta c \simeq -2 \Delta a$  it approximates to

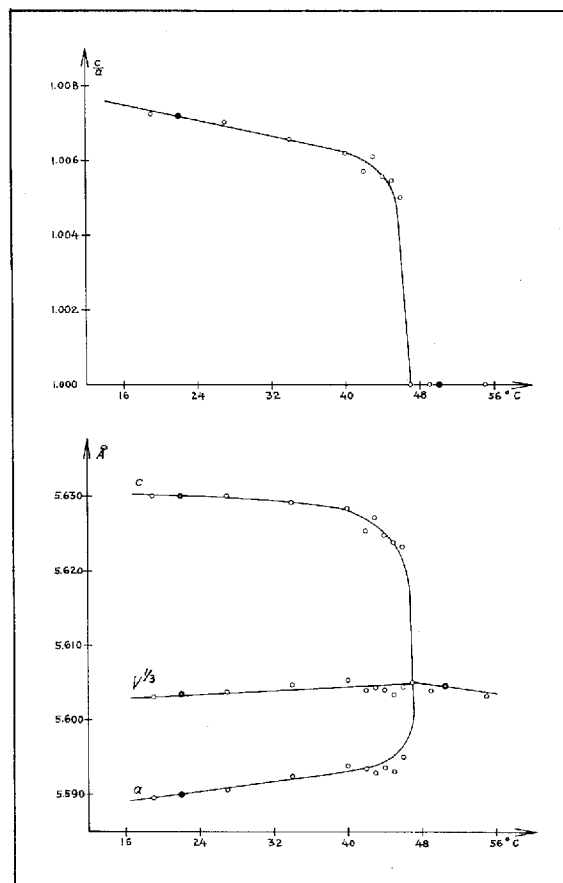
$$\Delta a = -1.06 a \cot \vartheta \cdot \Delta \vartheta \text{ and } \Delta c = -1.03 a \cot \vartheta \cdot \Delta \vartheta, \quad (3)$$

where, with sufficient accuracy,  $a \simeq c \simeq 5.60 \text{ \AA}$ , as the total uncertainty on  $\Delta a$  and  $\Delta c$  is of the order of 10 per cent.

Similarly the change of the axial ratio is given by

$$\Delta \left( \frac{c}{a} \right) = \frac{1}{a} (\Delta c - \Delta a). \quad (4)$$

The results obtained are shown in the graphs figs. 1 and 2, where the values of the axes at room temperature and at  $50^\circ C$ . have been adjusted so as to coincide with the values from the Guinier diagrams mentioned above. It appears that neither for  $CsPbCl_3$  is there any discernible change of the volume,  $V$ , at the transition point from the tetragonal to cubic struc-



Figs. 1 and 2. Axial ratio and unit cell dimensions as functions of temperature for  $\text{CsPbCl}_3$ ; solid circles refer to measurements from Guinier-diagrams.

ture. On the other hand it does look as if  $V^{1/3}$  plotted as a function of temperature changes abruptly at the transition point, which would imply that the coefficient of thermal expansion has a discontinuity there. Unfortunately our measurements are not accurate enough to make a definite statement.

A similar temperature dependence has been found for the axes of  $\text{BaTiO}_3$ ,<sup>1</sup> but here more recent experiments<sup>2</sup> have revealed that the curves near the transition point at 120°C. from tetragonal to cubic structure have

<sup>1</sup> H.D. MEGAW, Proc. Roy. Soc. A. London **189**, 261 (1947).

<sup>2</sup> H.F. Kay and P. VOUSDEN, Phil. Mag. Series 7, **40**, 1019 (1949).

discontinuities and also that thermal hysteresis plays a rôle. It is possible that a more refined technique will disclose similar irregularities also in the case of  $\text{CsPbCl}_3$ .

### Intensity measurements

In order to study the atomic arrangement in more detail, intensity measurements of the X-ray reflections on Weissenberg diagrams have been made on single crystals of  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$ , by means of  $\text{CuK}_\alpha$ -radiation. The reflections were photographed on sets of multiple films and relative intensities were visually estimated by comparison with an intensity scale prepared by taking a series of photographs of a particular reflection, each time increasing the exposure time by about 30 per cent. The intensities of these spots were then assumed to be proportional to their exposure times. Care was taken that X-ray intensity, temperature, speed of the Weissenberg motor, developer, fixer, and film material were kept as constant as possible. A new intensity scale was made for each crystal.

In order to check the reliability of this method two independent sets of measurements were made of the 0. and 1. layer lines of two different crystals of  $\text{CsPbCl}_3$  at room temperature. One had the dimensions  $100 \times 50 \times 40 \mu$  and the other  $100 \times 40 \times 30 \mu$ . The longest edge was the rotation axis. The agreement was found to be good, only in one case of 45 reflections measured was the deviation above 30 per cent, on an average it was about 12 per cent. of the measured intensity.

The reflections from a single crystal of  $\text{CsPbCl}_3$  (and similarly of  $\text{CsPbBr}_3$ ) were photographed with  $\text{CuK}_\alpha$ -radiation both at room temperature ( $20^\circ\text{C}$ .) and at 7—10 centigrades above the transition point on the same set of multiple films. This was achieved by displacing the film cylinder 3.0 mm in its carriage between the two exposures. In this way intensity changes which might be observed of the reflections, should be influenced least possible by film material and development. Heating and temperature control was performed as explained above. The "high-temperature" reflections gave small, well-defined spots on the film, with a uniform blackening. But on the room-temperature exposures of  $\text{CsPbBr}_3$ , these spots had broken up into 3—4 smaller spots lying close together, so that it was necessary to add up the intensities of the separate spots belonging to the same reflection. On heating the crystal to temperatures above  $130^\circ\text{C}$ . these spots again coalesced, showing that it is a reversible phenomenon. The reason for its occurrence is that when the crystals are cooled from temperatures where the unit cell is strictly cubic to room temperature the unit cell is slightly

modified by expansion of, say, the original  $a$ -axis and shrinkage of its two other axes. However, in other parts of the "single crystal" the expansion may be along the original  $b$  or  $c$ -axis (and shrinkage along the two others) and thus the result is a repeated twinning and microheterogeneity.<sup>1</sup> A similar effect could be observed on some of the diagrams of  $\text{CsPbCl}_3$ , but was there much less pronounced. For the particular crystal used it could also be inferred from the fact that on heating from room temperature to about  $55^\circ\text{C}$ . the reflections of type  $0k0$  were always displaced towards smaller, those of type  $00l$  towards higher  $\theta$ -values, that twinning could not be of major importance here.

The atomic scattering factors depend on the wavelength of the  $X$ -ray radiation used (dispersion), as do also the absorption corrections, and so it is conceivable that a more shortwaved radiation would give results different from those obtained with  $\text{CuK}_\alpha$ -radiation. Therefore photographs were also taken of  $\text{CsPbBr}_3$  at  $140^\circ\text{C}$ . with  $\text{MoK}_\alpha$ -radiation for intensity measurements.

Correction of the directly measured intensities for the Lorentz-polarization factors was made graphically as described by Cochran.<sup>2</sup> It was previously found that the absorption of  $X$ -radiation in  $\text{CsPbI}_3$  was compensated for by the temperature factor and could be included in the latter.<sup>3</sup> As this result presumably will also be valid here, we have made no direct corrections for the absorption. We thus finally obtain relative  $|F(hkl)|^2$ -values of which the uncertainty is assumed not to exceed 20–30 per cent.

As no piezoelectric effect has been detected in these crystals, neither with a dynamical<sup>4</sup> nor with a static method, it seems reasonable to conclude that they have centres of symmetry and consequently  $F(hkl) = \pm |F(hkl)|$ .

### Application of Fourier methods

With only one molecule  $\text{CsPbX}_3$  in a cubic unit cell the atomic positions should be determined by symmetry. Thus we may have:

$$\text{Pb in } (0, 0, 0); \text{ Cs in } \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right); \text{ X in } \left(\frac{1}{2}, 0, 0\right); \left(0, \frac{1}{2}, 0\right); \left(0, 0, \frac{1}{2}\right) \quad (\text{a})$$

$$\text{or Pb in } (0, 0, 0); \text{ Cs in } \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right); \text{ X in } \left(0, \frac{1}{2}, \frac{1}{2}\right); \left(\frac{1}{2}, 0, \frac{1}{2}\right); \left(\frac{1}{2}, \frac{1}{2}, 0\right). \quad (\text{b})$$

<sup>1</sup> Compare V. K. SEMENCHENKO, *J. Cryst. U.S.S.R.* 2, 145 (1957).

<sup>2</sup> W. COCHRAN, *J. Sci. Instr.* 25, No. 7 (1948).

<sup>3</sup> C. K. MÖLLER, loc. cit. p. 11.

<sup>4</sup> V. FRANK, Unpublished work.

Structure factors calculated on the basis of (a) with atomic scattering factors corrected for dispersion<sup>1</sup> do not give a very good agreement with the experimentally determined structure factors (Tables 3 and 4; Column 2 to be compared with Columns 4 and 5; see also figs. 8 and 9). The second possibility, (b), which is also equivalent to an interchange of Cs and Pb in (a), is even less satisfactory, and, furthermore, Pb would here acquire a coordination number 12, which seems rather unlikely.

Let us assume that Pb is correctly placed in (0, 0, 0), which is a centre of symmetry. As the atomic scattering factor of lead for the reflections of type  $0kl$  exceeds the sum of the atomic scattering factors of Cs and 3X, the structure factors  $F(0kl)$  must be positive. Hence we can calculate the electron projection on the  $bc$ -plane directly from the observed  $|F(0kl)|$ . This has been done for both  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$  above their transition temperatures, i. e. *in their cubic form*, and the result is shown in figs. 3 and 5.

It is seen that the electron clouds surrounding the halogen atoms are drawn out at right angles to the unit cell edges. As for the Cs-atoms, their peak heights come out much too low as compared with the peak height of the Pb-atoms, and on the projection of  $\text{CsPbCl}_3$  their electron clouds seem to have "spikes" towards the Cl-atoms.

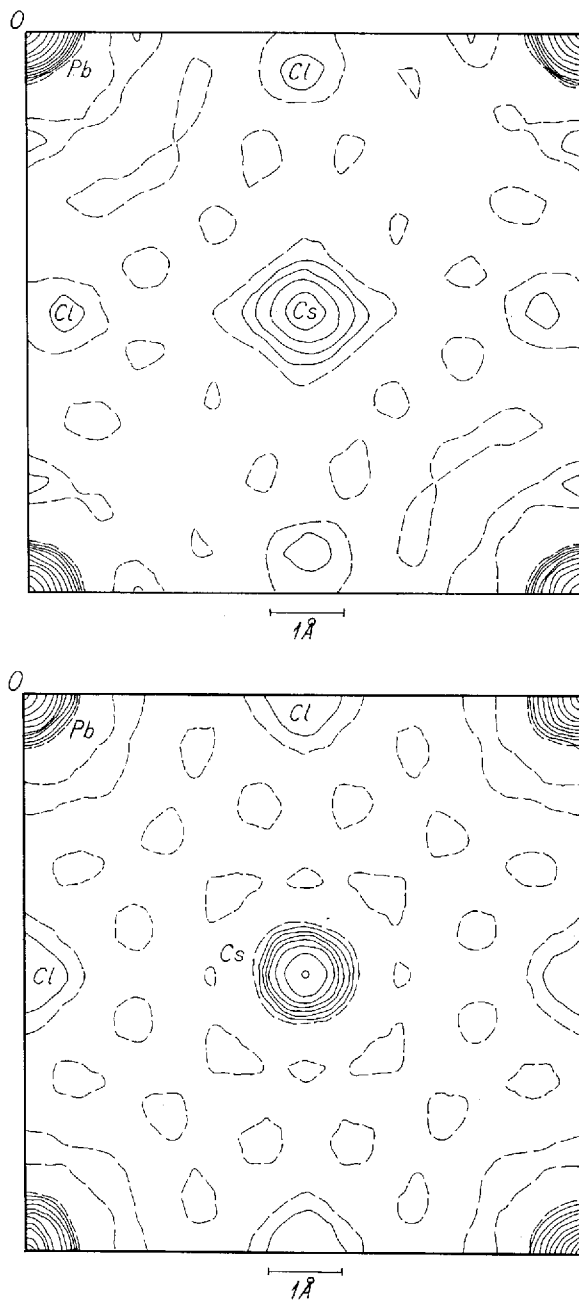
To estimate the contribution of diffraction effects to these somewhat unexpected results another projection on the  $bc$ -plane was calculated for  $\text{CsPbCl}_3$ , but now using the structure factors *calculated* for this compound with the atoms in position (a), instead of the observed  $F(0kl)$  as coefficients in the Fourier series.

This "theoretical" projection faithfully reproduces the atoms in the expected positions, and with reasonable peak heights. It is also seen that there is a definite correlation of the "diffraction errors" in figs. 3 and 4, and it seems evident that they cannot be made responsible for the peculiar features of the "experimental" projections.

An electron projection of  $\text{CsPbBr}_3$  calculated from structure factors obtained with  $\text{MoK}_\alpha$ -radiation gives mainly the same result as that based upon  $\text{CuK}_\alpha$ -radiation. It is thus unlikely that the latter kind of projection should be seriously distorted by dispersion and absorption. This conclusion gets further support from the fact that in the earlier work on  $\text{CsPbI}_3$ <sup>2</sup> the interpretation of the electron projections derived from intensities with  $\text{CuK}_\alpha$ -radiation was in no way obscured by any of the effects mentioned above, although they would be expected to be of greater importance in this case.

<sup>1</sup> Atomic scattering factors were taken from W. H. BRAGG and W. L. BRAGG, *The Crystal-line State*. Vol. I p. 330—333 (London 1949), corrections for dispersion from C. H. DAUBEN and D. H. TEMPLETON, *Acta Cryst.* 8, 841 (1955).

<sup>2</sup> C. K. MØLLER, *loc. cit.*



Figs. 3 and 4. Electron projections on (100) of cubic  $\text{CsPbCl}_3$  based on observed  $F(0kl)$  (top), and on  $F(0kl)$  calculated for ideal perovskite structure (bottom). The same relative scale has been used for the electron densities and contour lines have been drawn at the levels 0 (broken lines) 15, 30, 50, 75, 100, 150, 200, 250, 300, 350, and 400.

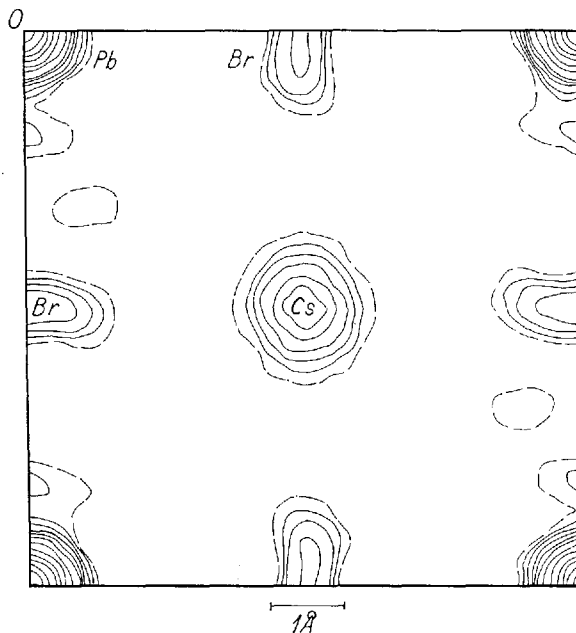


Fig. 5. Electron projection on (100) of cubic  $\text{CsPbBr}_3$ . Relative, arbitrary scale for electron density. Contour lines drawn as in figs. 3 and 4.

Finally a projection of tetragonal  $\text{CsPbCl}_3$  has been calculated from its observed  $|F(0kl)|$ . The result is almost indistinguishable from that of the cubic form. Difference synthesis with the Fourier-coefficients  $F(0kl)_{\text{tetr.}} - F(0kl)_{\text{cub.}}$  obtained from the experimentally determined intensities for the cubic and tetragonal modifications of both  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$  also show near identity of the two forms; in fact, the only observable changes in the electron distributions on going from the tetragonal to the cubic structures seem to be a reduction in peak height of the Cs-atoms and a small displacement of the halogen atoms towards the unit cell edges (about  $0.05 \text{ \AA}$  in  $\text{CsPbCl}_3$ ).

For the interpretation of the above results it should be remembered that an electron projection derived from experimental data represents a superposition of the electron distributions in a huge number of unit cells. We have so far been referring structures to the small unit cells given in Tables 1 and 2. The existence of a superstructure below the transition temperatures shows that this cannot be correct for the tetragonal form, but above the transition points both optical and X-ray evidence compel us to accept the

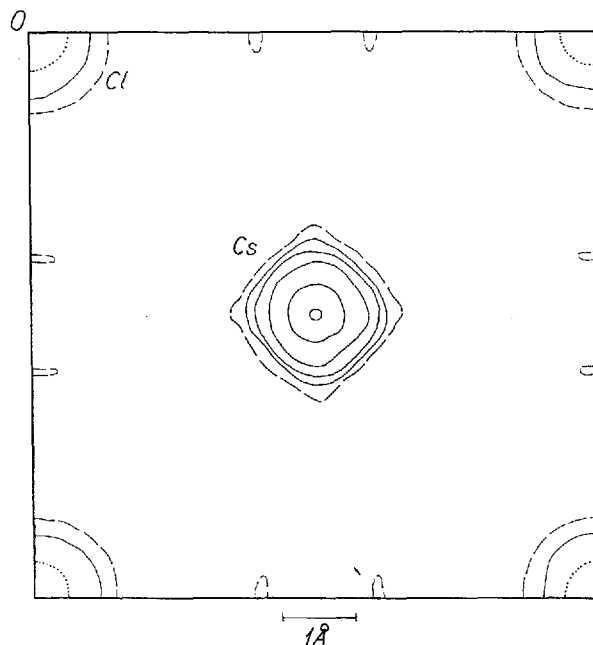


Fig. 6. Experimental electron density in the plane  $x = \frac{1}{2}$  of cubic  $\text{CsPbCl}_3$ . Contour lines are drawn at the levels 5 (broken line), 10, 15, 30, 60, and  $90 \text{ e}/\text{\AA}^3$ . The dotted lines near the corners indicate the maximum electron density in the Cl-regions (nearly  $15 \text{ e}/\text{\AA}^3$ ).

small unit cell combined with cubic symmetry. That the halogen peaks do not appear in the expected ideal positions (a) in projections of the latter may then either be explained as a result of the thermal movements, or we may assume that the true potential minima for Cs and the halogen atoms do not coincide with the ideal sites given in (a). Due to the limitations in resolution we cannot see the Cs- or Br-atoms in these subsidiary minima as separated peaks on the projections. Nor will it be possible to distinguish between the two mentioned possibilities from X-ray work alone.

To be more specific we shall assume that each Cl-(or Br-)atom in the unit cell has the choice between four potential minima lying along diagonals in sections perpendicular to the unit cell edges, about  $0.5 \text{ \AA}$  away from the "ideal positions", and similarly that Cs can "choose" between 6 (or 12) minima displaced about  $0.5 \text{ \AA}$  from the centre of the unit cell. Above the transition temperatures the kinetic energy of these atoms is higher than their mutual interaction energy, and there will be a constant diffusion of a halogen atom or a Cs-atom from one of its "private" potential minima

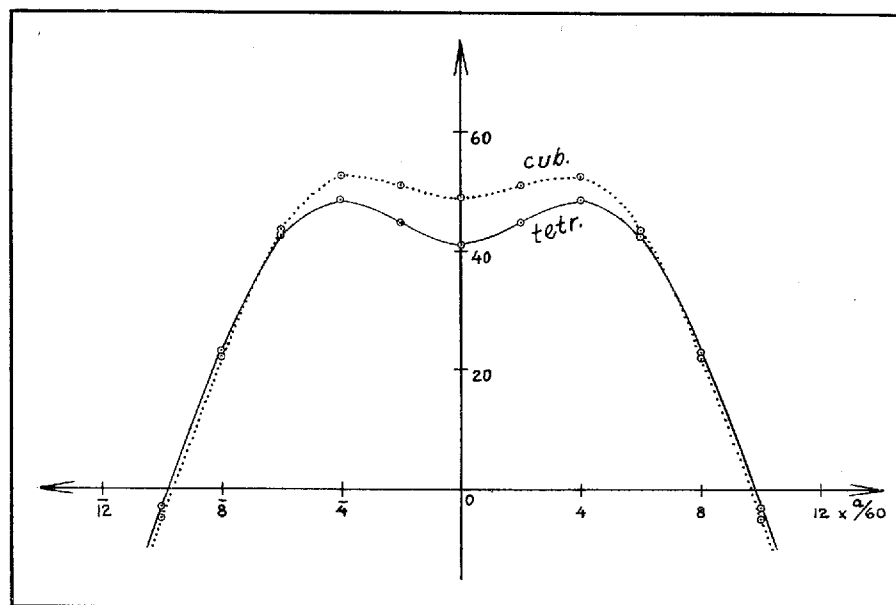


Fig. 7. Variation of the electron density along a radius vector from O in the plane  $x = \frac{1}{2}$  of  $\text{CsPbCl}_3$ . (Unit for the electron density four times that in fig. 6).

to another, thus simulating free rotation around the unit cell axes. Below the transition points, on the other hand, their kinetic energies are too small to prevent their being locked up in a particular configuration.

On these assumptions structure factors have been calculated for both  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$  (see next section) and their signs have been transferred to the experimentally determined  $|F(hkl)|$ . Fourier syntheses of the electron distributions in the planes  $x = 0$  and  $x = \frac{1}{2}$  have been made with these coefficients for  $\text{CsPbCl}_3$ . The section through  $x = \frac{1}{2}$  is reproduced in fig. 6, where the dotted curves represent the maximum electron density in the Cl-atoms. Fig. 7 represents a plot of the electron density along a radius vector from the unit cell corner in this section and illustrates how small the differences are between the tetragonal and the cubic form in this respect.

Three-dimensional difference syntheses in these planes have also been calculated, but apart from confirming the above observations they show nothing new.

### Comparison of calculated and observed structure factors

Further evidence that the assumption of random distribution of the Cs- and the halogen atoms on certain selected sites is compatible with the X-ray work comes from a comparison of calculated and observed structure factors.

These calculations have been made on the basis of the formula

$$F(hkl) = \sum_i f_i(hkl) \cdot \cos 2\pi (hx_i + ky_i + lz_i), \quad (5)$$

where  $x_i, y_i, z_i$  are the atomic parameters,  $f_i$  the atomic scattering factors, and the summation is over all the atoms "i" in the unit cell. The  $f_i(hkl)$  have been obtained for the different reflections  $hkl$  by a graphical method and this may give rise to small errors of the order of a few per cent of the  $F(hkl)$ , which, however, is small as compared with the experimental uncertainty.

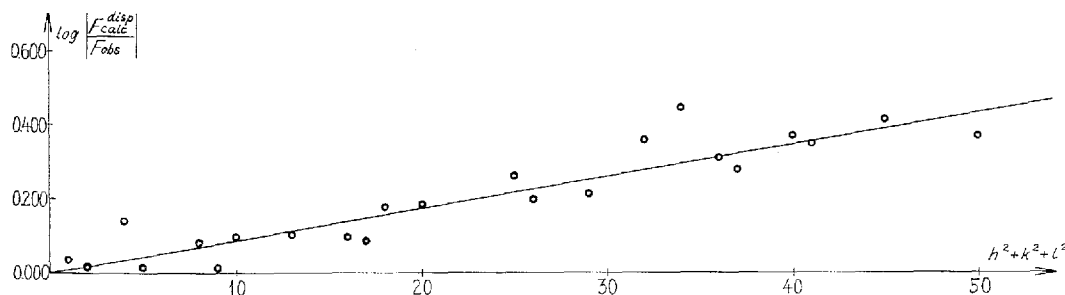
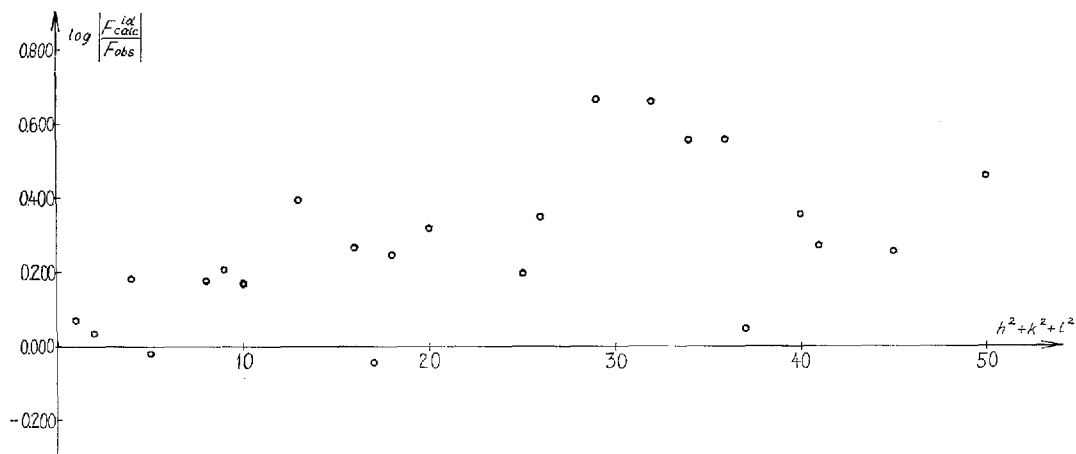
Nearly all the structure factors corresponding to reflections within the limiting sphere for  $\text{CuK}\alpha$ -radiation have been calculated for both  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$  with the atoms in the "ideal positions" (a) and isotropic atomic scattering factors, i.e.  $f(hkl) = f(\vartheta)$ . It is evident from Tables 3 and 4 that the structure factors calculated in this way are not in very good agreement with the experimental ones and in several places there are real discrepancies. The differences between weak and strong reflections are much less accentuated in the latter than in the former. Plots of  $\log \left| \frac{F_{calc.}^{id.}}{F_{obs.}} \right|$  against  $h^2 + k^2 + l^2$  should theoretically approach a straight line,<sup>1</sup> but this is not very obvious as seen from the example of  $\text{CsPbBr}_3$  in figs. 8 and 9.

Next we have calculated the structure factors on the assumption that the Cs- and halogen atoms are randomly displaced from their ideal positions. For the X-ray analysis it makes no difference whether the small displacements of the atoms are of a stationary character or whether they are caused by thermal vibrations of the lattice. This allows the two possibilities to be treated exactly alike and we can take over the whole treatment of the influence of thermal vibrations on the X-ray intensities.<sup>2</sup>

The result of these considerations is that if the displacement amplitude for the atoms of species "i" is given by the vector  $\mathbf{u} = u_x \mathbf{a} + u_y \mathbf{b} + u_z \mathbf{c}$ , their atomic scattering factor appropriate for the reflection  $hkl$  with X-ray radi-

<sup>1</sup> See e.g. H. LIPSON and W. COCHRAN, Determination of Crystal Structures, p. 61. London 1953.

<sup>2</sup> See e.g. R.W. JAMES, The Optical Principles of the Diffraction of X-Rays. Chapters I and V. London 1948.



0 layer line

Fig. 8.  $\log_{10} \left| \frac{F_{\text{calc}}}{F_{\text{obs}}} \right|$  versus  $h^2 + k^2 + l^2$  for the zeroth layer line of cubic CsPbBr<sub>3</sub>.

tion of wavelength  $\lambda$  should be multiplied by  $\exp \{-2 \pi^2 \overline{(\mathbf{S} \cdot \mathbf{u})^2}\}$ , where  $\overline{(\mathbf{S} \cdot \mathbf{u})^2}$  is  $\left( \frac{2 \sin \vartheta}{\lambda} \right)^2$  times the mean-square displacement parallel to the reciprocal vector  $\mathbf{S} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*$ .

For each halogen atom we have assumed four displaced positions as explained above. Hence, e.g. for the atom displaced  $u\sqrt{2}$  from the ideal position  $\left( \frac{1}{2}, 0, 0 \right)$  along the diagonals in the plane  $x = \frac{1}{2}$ , the "effective" atomic scattering factor becomes  $f(\vartheta) \exp \{-2 \pi^2 u^2 (k^2 + l^2)\}$ , and analogously for the two other halogen atoms by cyclic replacement. For the Cs-atoms we have assumed that there are six possible displacements  $\mathbf{U}$ , viz. towards the

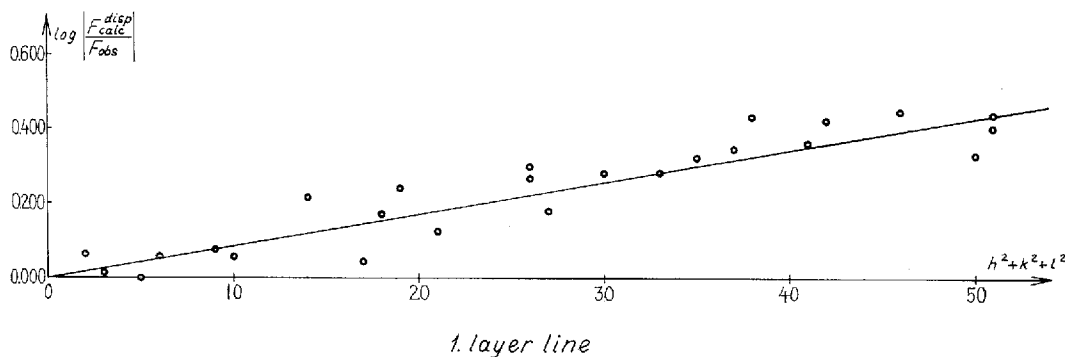
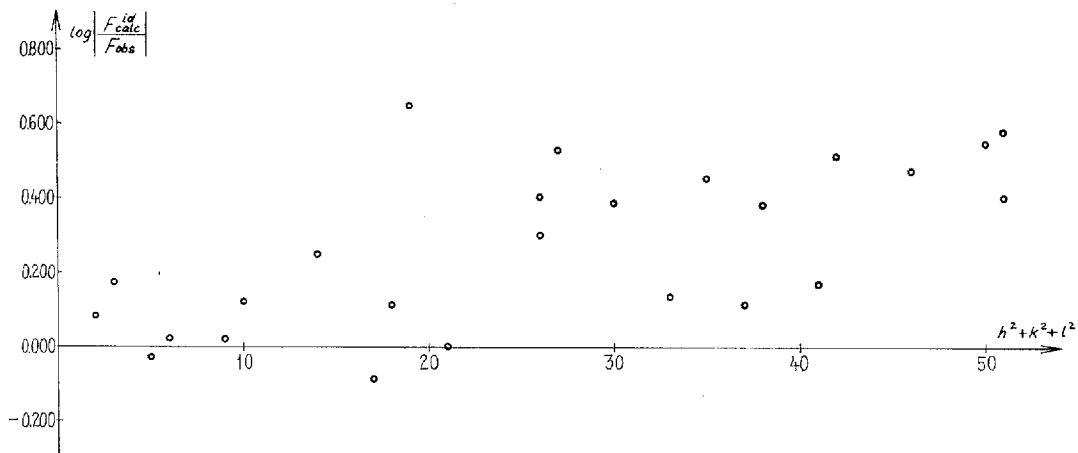


Fig. 9.  $\log_{10} \left| \frac{F_{\text{calc}}}{F_{\text{obs}}} \right|$  versus  $h^2 + k^2 + l^2$  for the first layer line of cubic  $\text{CsPbBr}_3$ .

centres of the unit-cell faces, but there might equally well be twelve such displacements towards the unit-cell edges. Formally this only changes the interpretation of  $U$ . Altogether the expression for the structure factor is then given by:

$$F(hkl) = f(\vartheta)_{\text{Pb}} + f(\vartheta)_{\text{Cs}} \cdot \exp \left\{ -\frac{2\pi^2 U^2}{3} (h^2 + k^2 + l^2) \right\} \cdot \cos \pi (h + k + l) \left. \begin{array}{l} \\ + f(\vartheta)_{\text{X}} [\exp \{ -2\pi^2 u^2 (k^2 + l^2) \} \cdot \cos \pi h + \exp \{ -2\pi^2 u^2 (h^2 + l^2) \} \cdot \cos \pi k \\ + \exp \{ -2\pi^2 u^2 (h^2 + k^2) \} \cdot \cos \pi l]; \end{array} \right\} \quad (6)$$

With this formula calculations of structure factors have been made for a certain range of values of  $u$  and  $U$ . The best agreement with the experi-

TABLE 3. Comparison of observed and calculated  $F$ -values for  $\text{CsPbCl}_3$ .  
(0., 1., 2., and 3. layer line)

Indices	Calculated $F$ -values		Observed $F$ -values				Indices	Calculated $F$ -values		Observed $F$ -values			
	Cubic structure		Cubic structure		Tetragonal structure			Cubic structure		Cubic structure		Tetragonal structure	
$hkl$	Ideal perovskite	Dis-placed perovskite	$F_{\text{obs.}}$ at about 54° C.	$F_{\text{obs.}}$ at temp. corr.	$F_{\text{obs.}}$ at about 20° C.	$F_{\text{obs.}}$ at temp. corr.	$hkl$	Ideal perovskite	Dis-placed perovskite	$F_{\text{obs.}}$ at about 54° C.	$F_{\text{obs.}}$ at temp. corr.	$F_{\text{obs.}}$ at about 20° C.	$F_{\text{obs.}}$ at temp. corr.
010	38	37	37	37	36	36	441	20	35	25	30	29	33
020	148	133	117	117	118	118	451	58	43	34	43	37	44
030	29	29	34	35	33	34	551	7	32	24	31	24	29
040	112	83	77	84	81	86							
050	23	27	25	29	24	26	012	32	38	32	33	33	34
060	89	55	46	56	49	57	022	130	108	96	100	92	95
070	18	27	24	31	26	32	032	27	32	33	36	36	38
110	103	100	91	91	89	89	042	104	72	69	77	70	75
120	32	38	38	38	39	40	052	22	29	28	33	28	32
130	85	74	65	68	67	70	062	86	50	41	51	45	53
140	26	40	42	46	39	42	112	93	91	81	83	84	86
150	66	49	53	62	48	53	122	29	38	39	40	41	42
160	20	40	35	42	33	39	132	79	69	64	69	66	69
170	56	35	28	37	33	41	142	24	38	38	42	39	42
220	130	107	93	96	94	97	152	64	47	41	48	44	50
230	27	32	31	33	31	32	162	19	37	30	37	31	36
240	104	72	62	69	61	67	222	119	91	85	90	80	85
250	22	29	25	30	21	23	232	25	34	33	36	30	32
260	86	50	39	49	42	49	242	99	64	54	62	58	64
330	74	61	49	54	53	57	252	21	31	25	30	28	32
340	22	35	28	32	33	37	262	84	47	38	47	40	48
350	62	46	37	44	42	48	332	70	57	48	54	50	54
360	19	36	25	32	25	30	342	22	35	29	34	29	33
440	92	54	39	47	44	50	352	60	44	34	42	41	47
450	19	32	25	32	29	34	362	18	34	25	33	28	34
550	56	40	34	44	39	48	442	89	50	39	48	38	44
							452	18	32	28	36	28	33
011	103	100	91	91	89	89	013	85	74	57	60	60	63
021	32	38	40	41	36	37	023	27	32	34	37	34	36
031	86	75	72	73	74	75	033	74	61	60	65	63	68
041	26	40	43	47	41	44	043	23	35	34	39	35	39
051	66	49	49	57	51	56	053	61	45	37	44	35	41
061	20	39	39	47	42	49	063	19	36	29	37	31	37
071	56	35	31	41	37	46	113	10	16	18	19	22	23
111	78	6	—	—	—	—	123	79	69	61	66	62	66
121	93	91	77	79	70	72	133	8	25	27	30	29	31
131	10	16	—	—	—	—	143	66	57	53	61	52	58
141	74	70	66	73	68	73	153	8	29	26	32	26	30
151	8	25	—	—	—	—	163	57	44	35	45	38	46
161	60	52	43	52	46	54	223	25	33	34	37	33	36
171	7	28	—	—	—	—	233	70	57	49	55	48	52
221	29	38	40	42	34	35	243	22	35	30	35	32	37
231	79	69	61	66	63	66	253	60	44	34	42	39	45
241	24	38	33	37	34	37	263	18	34	25	33	28	34
251	64	48	43	50	45	51	333	8	29	25	28	26	29
260	19	38	26	33	31	36	343	61	49	39	46	40	46
331	8	25	—	—	—	—	353	8	31	25	32	24	29
341	66	56	46	54	51	56	443	19	34	28	35	26	31
351	8	30	—	—	—	—	453	56	40	33	43	35	43
361	57	44	36	46	34	41							

TABLE 4. Comparison of observed and calculated  $F$ -values for  $\text{CsPbBr}_3$ . (0. and 1. layer line)

Indices	Calculated $F$ -values		Observed $F$ -values				Indices	Calculated $F$ -values		Observed $F$ -values			
	Ideal perovskite	Displaced perovskite	Cubic structure		Monoclinic structure			Ideal perovskite	Displaced perovskite	Cubic structure		Monoclinic structure	
$hkl$			$F_{\text{obs.}}$ at about 140° C.	$F_{\text{obs.}}$ at temp. corr.	$F_{\text{obs.}}$ at about 20° C.	$F_{\text{obs.}}$ at temp. corr.	$hkl$			$F_{\text{obs.}}$ at about 140° C.	$F_{\text{obs.}}$ at temp. corr.	$F_{\text{obs.}}$ at about 20° C.	$F_{\text{obs.}}$ at temp. corr.
010	54	50	46	47	48	49	011	86	82	71	74	76	78
020	192	170	126	136	128	137	021	47	50	50	55	51	55
030	42	27	26	31	23	26	031	74	63	56	68	52	60
040	145	100	79	109	96	124	041	37	50	45	64	46	59
050	33	19	—	—	—	—	051	58	43	23	39	31	45
060	116	65	32	67	47	81	061	28	48	22	46	18	32
070	26	20	—	—	—	—	071	49	29	14	37	—	—
110	88	84	81	84	95	97	111	64	44	43	46	46	48
120	47	50	49	54	53	57	121	79	86	75	85	79	86
130	74	63	50	62	59	69	131	38	3	—	—	—	—
140	37	51	41	58	49	64	141	65	75	50	73	65	85
150	58	41	26	44	32	47	151	36	17	11	20	—	—
160	28	48	25	53	31	54	161	53	59	22	47	40	70
170	49	29	14	(37)	21	46	171	30	22	8	22	—	—
220	172	133	110	130	126	142	221	43	48	41	49	50	57
230	39	33	26	34	24	30	231	69	65	39	51	55	68
240	137	84	55	83	58	79	241	34	46	34	52	46	63
250	31	25	15	28	15	23	251	56	43	23	42	38	60
260	112	57	24	55	27	51	261	28	43	19	43	—	—
330	65	55	37	53	37	48	331	40	16	9	13	—	—
340	33	39	21	36	24	34	341	58	58	29	50	41	60
350	54	42	15	30	23	38	351	34	25	12	24	—	—
360	27	40	15	38	19	37	361	50	48	17	44	24	48
440	120	59	26	50	24	39	441	30	39	22	42	49	80
450	26	30	14	32	13	25	451	52	43	16	38	—	—
550	49	39	17	46	18	40	551	30	31	12	35	—	—

mental  $|F(hkl)|$  is obtained with  $U = 0.075$  and  $u = 0.070$ ; the latter is also derived directly from the electron projection of  $\text{CsPbCl}_3$ . The corresponding displacements in Å-units are for  $\text{CsPbCl}_3$ : 0.42 Å and 0.39 Å; and for  $\text{CsPbBr}_3$  0.43<sub>5</sub> Å and 0.40<sub>5</sub> Å, respectively.

Plots of  $\log \left| \frac{F_{\text{calc.}}^{\text{disp.}}}{F_{\text{obs.}}} \right|$  against  $h^2 + k^2 + l^2$  now show rather good approximations to straight lines of the type

$$\log_{10} \left| \frac{F_{\text{calc.}}}{F_{\text{obs.}}} \right| = \log_{10} A + B \cdot (h^2 + k^2 + l^2), \quad (7)$$

where  $A$  and  $B$  are constants which can easily be evaluated from the graphs. The experimentally determined relative  $|F(hkl)|$ -values have then been brought on absolute scales corresponding to  $F(000) = 186$  for  $\text{CsPbCl}_3$  and  $F(000) = 234$  for  $\text{CsPbBr}_3$  by multiplication with the factors  $A$ . They are

given in Tables 3 and 4 in the 4th and 6th column. The last term in (7) is due to the isotropic thermal movements of the atoms but also includes the absorption correction. In order to eliminate its influence on the experimental  $F(hkl)$  they have finally been multiplied by the factor  $10^{B_{\text{cub}}(h^2+k^2+l^2)}$ . This final version of the observed structure factors, which is reproduced in Columns 5 and 7 of Table 3 and 4 shows almost perfect agreement with the structure factors calculated from (6), thus proving our assumptions to be appropriate.

Similar conversions and corrections have been applied to the structure factors measured for the tetragonal or monoclinic form of these crystals and the constants,  $B_{\text{tetr.}}$  have also been determined. As pointed out above, the intensities here are more difficult to measure, and hence there is a greater uncertainty on the  $F_{\text{exp.}}$ . However, the  $B_{\text{tetr.}}$ -values determined for different layer lines of the same crystal at constant temperature are identical within the accuracy of the measurements.

Although the  $B$ -values do include a term contributed from the absorption, the differences  $B_{\text{tetr.}} - B_{\text{cub.}}$  by our method of comparing the intensities depend only on the temperatures and the possible changes of the atomic arrangement. If we could be sure that only the changes in thermal movements of the atoms were of importance the following relation should be approximately true:<sup>1</sup>

$$\Delta B = 0.4343 \cdot \frac{3h^2 \cdot N}{2k\Theta_D^2} \cdot \frac{1}{Ma^2} \cdot \Delta T, \quad (8)$$

where  $\Theta_D$  is the "characteristic" or Debye-temperature. Inserting  $h = 6.623 \cdot 10^{-27}$ ,  $k = 1.380 \cdot 10^{-16}$ ,  $N = 6.025 \cdot 10^{23}$ , and rearranging we get with  $a$ , the unit-cell edge, in Å units:

$$\Theta_D = 35.32 \frac{1}{a} \left( \frac{1}{M} \cdot \frac{\Delta T}{\Delta B} \right)^{1/2} \quad (9)$$

In this formula  $M$  is the molecular weight of the vibrating particle; in our case we may presumably insert the molecular weight of the unit-cell contents, i.e.  $\text{CsPbX}_3$ , thus asking for a lower limit of  $\Theta_D$  and considering the influence of the acoustic waves only.

Neglecting the existence of the superstructure we can then calculate the  $\Theta_D$  compatible with the decrease in intensity of the X-ray reflections

<sup>1</sup> Cf. R.W. JAMES, loc. cit. p. 219-38.

on heating the crystals from room temperature to above their transition points, the results being

$$\Theta_D = 72^\circ K \text{ for CsPbCl}_3 \text{ and } \Theta_D = 60^\circ K \text{ for CsPbBr}_3.$$

As the characteristic temperatures obtained in this way do not seem unreasonable these calculations indicate that very little happens to the atoms at the transition from cubic to tetragonal structure apart from their preferred occupation of one particular set of their possible potential minima.

On the same assumption we may also estimate an average value for the root-mean-square displacements of the atoms, due to thermal movements, from the approximate formula:

$$\sqrt{u^2} \simeq \frac{a}{\pi} \sqrt{\frac{3}{0.8686} \cdot \frac{\Delta B}{\Delta T} \cdot T} \quad (10)$$

We find for CsPbCl<sub>3</sub>  $\sqrt{u^2} \simeq 0.25 \text{ \AA}$ , and for CsPbBr<sub>3</sub>  $\sqrt{u^2} \simeq 0.28 \text{ \AA}$  – values which seem quite reasonable.

### Discussion

One of the aims of the present investigations was to determine the configuration of the lead-halogen complexes, and at first sight it seemed that a very good argument could be given for the regular octahedron from the existence of perovskite-like structures with one molecule CsPbX<sub>3</sub> in the unit cell. However, the X-ray analysis shows that this cannot be true, and if we accept the interpretation given above, it seems doubtful whether it is at all possible to speak of a fixed configuration of a particular PbX<sub>6</sub>-unit, — or indeed of such units, in the cubic crystals.

In the tetragonal crystals, on the other hand, it appears that there is a fixed configuration, but this is not that of a regular octahedron although it is closely related to it. It is interesting that distorted PbX<sub>6</sub>-octahedra are also found in the yellow, orthorhombic CsPbI<sub>3</sub> and in the compounds Cs<sub>4</sub>PbX<sub>6</sub>.<sup>1</sup>

Although the displacements of the atoms from their ideal positions in the cubic crystals could have been described in terms of thermal movements we have here preferred to assume the existence of several possible potential minima for the Cs and X-toms, because the vibrational amplitudes in the

<sup>1</sup> C. K. MÖLLER. To be published in this series.

former description become rather large. Nor can we exclude the possibility of free rotations of these atoms in the cubic crystals, but whenever this has been assumed to explain certain transition phenomena in crystals, it has been shown that they may equally well, if not better, be explained by order-disorder transformations.<sup>1</sup>

It is tried to get a decision of this question from measurement of the entropy change at the transformation  $(\text{CsPbCl}_3)_{\text{tet.}} \rightleftharpoons (\text{CsPbCl}_3)_{\text{cub.}}$ .

On the above assumption there cannot be one single characteristic Cs-X distance in the cubic crystals, but rather a certain range of discrete values. The Pb-X distances on the other hand are well-defined, but they are considerably shorter than the distances to be expected from the sum of ionic radii.<sup>2</sup> (See Table 5).

This has also been observed for other crystals which contain lead and halogen atoms, and it may mean either that the ionic radius for Pb needs a revision or (more likely) that polarization ("covalency") is of importance in these compounds. The colour of the crystals also strongly suggests the latter explanation.

On the whole the perovskite-like crystals of the type  $\text{CsPbX}_3$  show so many analogies to the crystals of mixed oxides of the  $\text{BaTiO}_3$ -type that it is tempting to apply also to the latter the interpretation given here of the transformation from tetragonal to cubic structure. In this way there would be a close analogy of dielectric phenomena in solids to those in gases: The situation at temperatures above the transition to cubic structure where "free" diffusion of anions and some cations among selected potential minima creates a structure with maximum disorder of the kind described above, corresponds to a polar gas at very high temperatures in a very weak electric field (no orientation). Below the transition temperature the preferred occupation of certain potential minima (also present in the cubic state) may result in a multiple cell with no dipole moment, in which case we have an anti-ferroelectric phase. This corresponds to a non-polar gas of associated dipolar molecules (internal compensation). — Or the result of the transformation may be a unit cell with a dipole moment, whose electric field will help to create a preferred configuration all through the crystal, thus giving a ferroelectric. The analogy here, of course, is a gas of polar molecules in an electric field and at not too high temperatures.

Based on ideas of this kind MASON and MATTHIAS<sup>3</sup> have developed a

<sup>1</sup> J. FRENKEL, Kinetic Theory of Liquids. Chapter II. Oxford 1948. See also J. P. MATHIEU, Yearbook. Phys. Soc. G.B., 23—29 (1956).

<sup>2</sup> LANDOLT-BÖRNSTEIN, I. Band, 4. Teil p. 523.

<sup>3</sup> W. P. MASON and B. T. MATHIAS, Phys. Rev. 74, 1622 (1948).

TABLE 5. Some interatomic distances in the perovskite-like crystals of  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$

	Pb-X	Cs-X <sub>max.</sub>	Cs-X <sub>prob.</sub>	Cs-X <sub>min.</sub>	
$\text{CsPbCl}_3$ {	From the present work . . . . .	2.86 Å	3.76 Å	3.68 Å	3.13 Å
	From Pauling's ionic radii . . . . .	3.02 -		3.50 -	
	From Goldschmidt's ionic radii . . . . .	3.13 -		3.48 -	
$\text{CsPbBr}_3$ {	From the present work . . . . .	2.99 -	3.94 -	3.85 -	3.28 -
	From Pauling's ionic radii . . . . .	3.16 -		3.64 -	
	From Goldschmidt's ionic radii . . . . .	3.28 -		3.63 -	

theory for ferroelectricity in  $\text{BaTiO}_3$  which, however, has been severely criticized by JAYNES<sup>1</sup> mainly for the following reason. An order-disorder transition involving 6 close-lying Ti-positions (as assumed by MASON and MATTHIAS) will require an entropy change  $R \log 6 \simeq 3.6 \text{ cal mol}^{-1} \text{ deg}^{-1}$ , but the measured value is only about  $0.1 \text{ cal mol}^{-1} \text{ deg}^{-1}$ . However, it does not seem quite obvious how the entropy measurements should be interpreted, nor whether the simple calculation of the entropy is strictly valid. It is hoped that measurement of the corresponding entropy change in  $\text{CsPbCl}_3$  may help to clarify some of these problems, and it is also suggested that it might be interesting to make a thorough neutron or X-ray investigation of  $\text{BaTiO}_3$  at temperatures above  $120^\circ\text{C}$ .

### Acknowledgements

I wish to thank Professor A. TOVBORG JENSEN, Ph. D., for his interest in this work and Mr. PETER COLDING JØRGENSEN for carrying out many of the calculations and measurements.

<sup>1</sup> For a survey and references see H.D. MEGAW, Ferroelectricity in crystals, Chapter 10. Methuen, London 1957.

