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Debye–Waller factors of cesium chloride.

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Single crystals of cesium chloride with cube faces of about 4 × 5 mm were grown from aqueous solution. One of these was mounted on a General Electric XRD-5 single-crystal orienter and the integrated intensities of nine $h00$ reflections from the cube face were measured at 25 °C. Zirconium-filtered Mo K radiation was used in conjunction with a scintillation-counter detector and pulse-height analysis of the diffracted radiation. Only reflections in which the crystal intercepted the entire incident beam were measured. The background measured on both sides of the peaks was averaged and subtracted from the total number of counts accumulated in a $\theta-2\theta$ scan.

A plot of the logarithms of the ratios of the observed and calculated structure factors as a function of $\sin^2\theta/\lambda^2$ is shown in Fig. 1.

The experimental measurements were analyzed in the usual way to obtain the temperature factors of the individual atoms with the aid of the Busing–Levy least-squares program (Busing & Levy, 1962). Two calculations were carried out; in one (set 1, Table 1) the atomic scattering factors were corrected for dispersion effects with the use of corrections calculated by Dauben & Templeton (*International Tables for X-Ray Crystallography,* 1962), in the other (set 2, Table 1) no dispersion corrections were applied. The discrepancy coefficient, R, was 1·9 % in both cases and the Debye–Waller factors obtained from the two calculations did not differ significantly.

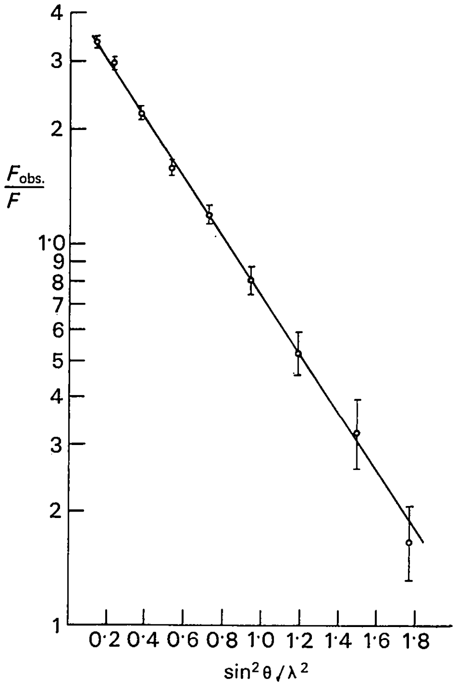

Fig. 1. F_{obs}/F as a function of $\sin^2\theta/\lambda^2$. $F=f_{\text{Cs}}+f_{\text{Cl}}[\pi i(h+k+l)]$ The indicated errors are statistical.

Table 1. *Influence of correction for dispersion effects on calculated values of Debye–Waller factors*

	Set 1 (including dispersion corrections)		Set 2 (no dispersion corrections)	
hkl	F_{obs}	F_{calc}	F_{obs}	F_{calc}
400	49·6	49·1	49·9	49·4
500	20·4	19·9	20·5	20·1
600	21·1	22·1	21·2	22·2
700	8·24	8·25	8·29	8·30
800	8·28	8·12	8·32	8·17
900	2·93	2·91	2·94	2·92
10 0 0	2·55	2·47	2·56	2·50
11 0 0	0·78	0·85	0·78	0·89
Scale factor	0·218 ± 0·005		0·216 ± 0·005	
B(Cl)	1·81 ± 0·08 Å^2		1·77 ± 0·07 Å^2	
B(Cs)	1·79 ± 0·03		1·81 ± 0·03	

The Debye–Waller factors of the individual atoms were found to be equal within experimental error:

$$B(\text{Cl}) = 1{\cdot}81 \pm 0{\cdot}08 \text{ Å}^2$$
$$B(\text{Cs}) = 1{\cdot}79 \pm 0{\cdot}03$$

The corresponding root mean-square amplitudes of thermal motion, obtained from the relation $B = 8\pi^2\overline{u^2}$, are:

$$[\overline{u^2}(\text{Cl})]^{\frac{1}{2}} = 0{\cdot}151 \pm 0{\cdot}003 \text{ Å}$$
$$[\overline{u^2}(\text{Cs})]^{\frac{1}{2}} = 0{\cdot}150 \pm 0{\cdot}001$$

The equality of the mean-square amplitudes of cesium and chlorine confirms the predictions of Waller, quoted by Blackman (1956), to the effect that for alkali halides at high temperatures the sum (in brackets) over the normal vibrations in the expression

$$\overline{u^2_{pq}} = \frac{kT}{m_p}\left[\sum_j \frac{(e^j_{pq})^2}{\omega_j^2}\right]$$

will be proportional to the mass of the atom; *i.e.* the mean-square amplitude $\overline{u^2_{pq}}$ is independent of the mass of the atoms, depending only on the forces between them. This is also borne out by the experimental values of the Debye–Waller factors of other alkali halides, in particular RbCl, KCl and CsI (Wasastjerna, 1946). Appreciable differences between the Debye–Waller factors of the individual atoms in alkali halides have apparently only been observed in cases where the measurements were carried out close to or below the Debye temperature (Lonsdale, *International Tables for X-Ray Crystallography,* 1962). Our measurements were made at 298 °K which can be regarded as a 'high temperature' since it is almost twice the Debye temperature.

The relation between the Debye–Waller factor and the Debye temperature, Θ, for cubic crystals consisting of one kind of atom only,

$$B = \frac{6h^2}{km\Theta}\left[\frac{\varphi(\Theta/T)}{\Theta/T} + \frac{1}{4}\right],$$

where B is taken to be the average of B(Cl) and B(Cs) and m is the average atomic weight of cesium and chlorine (Lonsdale, 1948), yields a value of 151°K for the Debye temperature of cesium chloride. A Debye temperature of 166°K has been calculated from the elastic constants assuming a nearest-neighbor interaction (Liebfried, 1955). The discrepancy between the two values is connected with the general relation $\Theta(X\text{-ray})/\Theta_D$ (elastic) < 1, due to the existence of low-frequency peaks in the vibrational spectrum (Blackman, 1956).

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Note on anomalous dispersion and Evans's X-ray study of tetragonal barium titanate.*

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Recently Chandrasekaran & Mohanlal (1965) have commented on the rather large effects of anomalous dispersion to be expected in violation of Friedel's law, which were not considered in my study (Evans, 1961) of the crystal structure of tetragonal barium titanate. The authors were kind enough to send me a preprint of their article and I was able to check their predictions against my original data. I measured with the Geiger counter all four equivalent reflections $h0l$, $\bar{h}0l$, $h0\bar{l}$, and $\bar{h}0l$. Unfortunately, I could find no variations in these measurements that would in any way correspond to those predicted by Chandrasekaran & Mohanlal. The explanation for this lack of observed effect probably lies in antiparallel twinning in the specimen that I used. If such twinning is present, although it is safe to assume that there will be little or no diffraction coherence between twin domains, the intensity variations between $+l$ and $-l$ will, of course, tend to average out.

The common presence of antiparallel twinning on (001), though difficult to demonstrate, has been revealed, among others, by Hooton & Merz (1955) using etching techniques, by Pearson & Feldman (1959) using powder-dusting techniques, and by Miller & Savage (1959) using optical strain techniques. Recently, Niizeki & Hasegawa (1965) have used the difference in intensity between the 003 and 00$\bar{3}$ reflections in Cr $K\alpha$ radiation in applying the Lang topographic technique to reveal the antiparallel twin domains in tetragonal barium titanate. Incidentally, their measurements of intensity variations resulting from anomalous dispersion in the 001, 002 and 003 reflections in Cr $K\alpha$ radiation are not in accord with the structure model proposed by Frazer, Danner & Pepinsky (1955), but do support (although they do not prove) that offered by Megaw (1962) based on Evans's study.

An intensive investigation of the anomalous dispersion effect in barium titanate crystals polarized in an electric field could go a long way to overcome the indeterminacy of the structure resulting from the instability of the structure factor functions (Evans, 1961), which has so far prevented a proper refinement of this structure. Unfortunately, I will not be able to carry out any further such studies on barium titanate.

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