subset first. This procedure insures maximum self-consistency within the subset of interest.

Other implications also arise. Suppose that as one monitors the several standard reflections, one finds significantly divergent behavior resulting in increasing $S^2(K)$. What might one choose to do short of mounting a fresh crystal? Perhaps the data can be significantly improved by measuring backgrounds for shorter periods and/or by using faster scan rates. The answers to such questions lie in the intelligent use of standard analysis as a feedback loop in experimental design. It is not hard to imagine in this age of mini-computer-controlled experiments a diffractometer programmed to ask and answer such questions.

The authors wish to thank V. Schomaker and L. H. Jensen for encouragement during the early part of this work. E. C. Lingafelter, G. J. B. Williams and J. P. Glusker read manuscripts, gave support, and offered valuable suggestions and criticism. G. J. B. W. suggested the title and also gave accounts of similar work performed by himself and J. Sygusch. We thank E. C. Lingafelter, H. Warren Smith, and N. J. Rose for the use of their standards. One of us (L.C.A.) wishes to acknowledge the U.S. Atomic Energy Commission under whose auspices some of this work was performed.

References

Abrahams, S. C. (1973). *Acta Cryst.* A**29**, 111–116.
Ammon, H. L., Watts, P. H. & Stewart, J. M. (1970). *Acta Cryst.* B**26**, 1079–1088.
Arndt, U. W. & Willis, B. T. M. (1966). *Single Crystal Diffractometry*, p. 268. Cambridge Univ. Press.
Busing, W. A. & Levy, H. A. (1957). *J. Chem. Phys.* **26**, 563–568.
Corfield, P. W. R., Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 197–204.
Ibers, J. A. (1969). *Acta Cryst.* B**25**, 1667–1668.
McGinnety, J. A., Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 2243–2250.
Peterson, S. W. & Levy, H. A. (1957). *Acta Cryst.* **10**, 70–76.
Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination.* New York: Macmillan.

Acta Cryst. (1975). A**31**, 249

The Debye–Waller Factors of the Rubidium and Cesium Halides

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(*Received* 9 *July* 1974; *accepted* 8 *November* 1974)

Computed mean-square displacements and Debye–Waller B_K factors, derived using the deformation dipole model, are reported for the rubidium and cesium halides at 4·2, 80, and 300°K. Experimental X-ray diffraction Debye–Waller factors, obtained at 300°K, are reported for CsCl, CsBr, and CsI. The calculated B_K values are compared with these and other experimental values wherever such data exist. The differences between calculated and measured values at 4·2°K are not large but in three out of four cases lie outside the small experimental uncertainties quoted. At 300°K, on the other hand, the differences tend to be larger, but in about half of the cases are less than the experimental uncertainty.

Introduction

The mean-square displacements of ions in the rubidium halides have been calculated by Govindarajan (1973) using a shell model where 11 to 14 parameters are fitted to the measured phonon dispersion curves. The Debye–Waller factors have not so far been measured for all of these eight crystals. However, Hafemeister, De Pasquali & De Waard (1964) have measured the recoilless fraction f_a for the I^- ion in several alkali halide crystals at 80°K using the Mössbauer effect, and Boyle & Perlow (1966) have made similar measurements at 4·2°K for the Cs^+ ion in the cesium halides. Barnea & Post (1966) have measured B_K values for Cs^+ and Cl^- ions in CsCl. Recently Beaver & Weymouth (Beaver, 1974) have measured B_K values on powder samples of CsCl, CsBr, and CsI at 300°K using X-ray diffraction measurements.

The purpose of this paper is to compare the measured values and computed values that are based on lattice-dynamical models which have fewer parameters, and fit the dispersion curves equally well. Moreover the parameters are determined mainly by fitting to macroscopic data (*e.g.*, static and high-frequency dielectric constants). Thus, although the calculated dispersion curves are mainly theoretical predictions, their agreement with experiment indicates that the models are producing dynamical matrices which are probably good for any phonon wave vector and not merely for those lying along a restricted class of high-symmetry directions. Our calculations are based on the eigendata derived from various deformation dipole (DD) models. In case of RbCl, RbBr, and RbI (Agrawal & Hardy, 1975) and CsCl, CsBr, and CsI (Agrawal & Hardy, 1974) five parameters are used, while in the case of RbF and CsF we use the model of Cunningham, Sharma, Jaswal, Hass & Hardy (1974) which has eight parameters.

Theory

The decrease in the intensity of Bragg reflections with an increase in temperature is determined by the factor exp $(-2W_K)$ which is known as the Debye–Waller Factor (DWF) of the Kth ion in the unit cell. For cubic crystals, within the harmonic approximation this can be written in terms of the mean-square displacements $\langle U_K^2\rangle$ of the ion as

$$\begin{aligned} 2W_K &= \frac{16\pi^2\langle U_K^2\rangle}{3\lambda^2}\sin^2\theta \\ &= \frac{2B_K\sin^2\theta}{\lambda^2}\,. \end{aligned} \qquad (1)$$

In this expression λ is the wavelength of the incident radiation and 2θ is the angle of scattering.

The recoilless fraction f_K measured in the Mössbauer measurements is equal to the Debye–Waller factor. In this case equation (1) can be written as $2W_K = \langle(\mathbf{k}\,.\,\mathbf{U}_K)^2\rangle$, or alternatively

$$\begin{aligned} 2W_K &= \frac{4\pi^2}{3\lambda^2}\langle U_K^2\rangle \\ &= \frac{B_K}{2\lambda^2} \end{aligned} \qquad (2)$$

where $\mathbf{k}$ is the wave vector of the emitted γ radiation and λ is its wavelength.

In the harmonic approximation the mean-square displacement of the Kth ion in a unit cell in a perfect cubic crystal is given by the relation (Maradudin, Montroll, Weiss & Ipatova, 1971)

$$U_K^2 = \sum_{\mathbf{q}j} \frac{\hbar|\sigma_K(\mathbf{q}|j)|^2}{NM_K\omega_j(\mathbf{q})}\{n[\omega_j(\mathbf{q})]+\tfrac{1}{2}\}\,. \qquad (3)$$

In equation (3) $\sigma_K(\mathbf{q}|j)$ and $\omega_j(\mathbf{q})$ are the eigenvector and eigenfrequency, respectively, corresponding to wave vector $\mathbf{q}$ and branch index j, $\hbar$ is Planck's constant divided by 2π, M_K is the mass of the Kth type of ion in the unit cell, N is the number of unit cells in the crystal and $n[\omega_j(\mathbf{q})]$ is the Bose–Einstein occupation number for an oscillator of angular frequency $\omega_j(\mathbf{q})$.

Experimental results

Experimental results on the B_K factors of CsCl, CsBr, and CsI will be briefly described here [a more complete discussion may be found elsewhere (Beaver, 1974)].

Integrated intensity measurements for powder samples were made at room temperature. Two X-ray diffraction systems were used, a Philips diffractometer with a flat-plate post-monochromator and a Picker diffractometer with a doubly bent pre-monochromator. In each case the polarization ratio was measured. All measurements were made with Cu $K\alpha$ X-rays. The samples were prepared three different ways, loose powder, powder mixed with paraffin and powder packed under pressure. The packed powder samples were rejected because of preferred orientation.

The integrated intensities were fitted to values calculated for the flat powder sample case (James, 1965)

Table 1. *Mean-square displacements of the ions in rubidium halides in units of* Å^2

Temperature	RbF		RbCl		RbBr		RbI	
	$\langle U^2\rangle$Rb$^+$	$\langle U^2\rangle$F$^-$	$\langle U^2\rangle$Rb$^+$	$\langle U^2\rangle$Cl$^-$	$\langle U^2\rangle$Rb$^+$	$\langle U^2\rangle$Br$^-$	$\langle U^2\rangle$Rb$^+$	$\langle U^2\rangle$I$^-$
4·2°K*	0·00770	0·01635	0·00925	0·01401	0·00967	0·00996	0·01049	0·08784
80°K†	0·01571	0·02252	0·02251	0·02567	0·02537	0·02548	0·03072	0·02970
	(0·01590)	(0·02224)	(0·02252)	(0·02530)	(0·02519)	(0·02673)	(0·03143)	(0·02856)
300°K†	0·05304	0·06100	0·08226	0·08266	0·09427	0·09192	0·11793	0·11152
	(0·05918)	(0·06599)	(0·08779)	(0·09039)	(0·10030)	(0·10563)	(0·12997)	(0·12005)

* The values of $\langle U_K^2\rangle$ shown have been derived using 80°K eigendata.
† The values shown in the brackets are those calculated by Govindarajan (1973).

Table 2. *Mean-square displacements of the ions in cesium halides in units of* Å^2

Temperature	CsF		CsCl		CsBr		CsI	
	$\langle U^2\rangle$Cs$^+$	$\langle U^2\rangle$F$^-$	$\langle U^2\rangle$Cs$^+$	$\langle U^2\rangle$Cl$^-$	$\langle U^2\rangle$Cs$^+$	$\langle U^2\rangle$Br$^-$	$\langle U^2\rangle$Cs$^+$	$\langle U^2\rangle$I$^-$
4·2°K*	0·00711	0·01877	0·00733	0·01353	0·00768	0·00963	0·00809	0·00813
80°K	0·01945	0·02770	0·01997	0·02243	0·02189	0·02214	0·02453	0·02377
300°K	0·06901	0·07955	0·07501	0·07431	0·08046	0·07901	0·08979	0·08666

* The values of $\langle U_K^2\rangle$ shown here at 4·2°K have been derived using 80°K eigendata.

using atomic scattering factors calculated by Cromer & Mann (1968). The scattering factors were corrected for dispersion. The integrated intensities were corrected for thermal diffuse scattering using the first-order correction of Chipman & Paskin (1959). The fitting program treated the two B factors and the incident intensity as fitting parameters.

The results reported in Table 3 are, in each case, obtained from three independent determinations using both X-ray systems and both types of samples. In the case of CsCl and CsBr, 13 to 18 reflections were used. In the case of CsI, 7 to 8 reflections were used. The uncertainties quoted in Table 3 are, in each case, the standard error (of the mean) for each group of three determinations. Thus, these uncertainties are a best estimate of random errors, but do not attempt to include possible systematic errors.

Table 3. *Theoretical and experimental Debye–Waller B_K factors for the rubidium and cesium halides*

Ions	Temperature	F^-		Cl^-		Br^-		I^-		References (Experimental values)
		$B(+)$	$B(-)$	$B(+)$	$B(-)$	$B(+)$	$B(-)$	$B(+)$	$B(-)$	
Rb^+	4·2°K*	0·2025	0·4304	0·2435	0·3674	0·2545	0·2621	0·2761	0·2297	
	80°K	0·4133	0·5928	0·5924	0·6756	0·6678	0·6707	0·8084	0·7816	
									(0·628 ± 0·124)	Hafemeister *et al.* (1964) (Area method)
	300°K	1·3959	1·6054	2·1649	2·1754	2·4811	2·4193	3·1037	2·9351	
				(2·28 ± 0·1)	(2·44 ± 0·1)					Jarvinen & Inkinen (1967) (X-ray)
Cs^+	4·2°K*	0·1870	0·4940	0·1929	0·3561	0·2020	0·2534	0·2128	0·2140	
		(0·1949 ± 0·0020)		(0·1992 ± 0·0020)		(0·2026 ± 0·0025)		(0·2196 ± 0·0038)		Boyle & Perlow (1966)
	80°K	0·5118	0·7291	0·5254	0·5902	0·5761	0·5827	0·6458	0·6257	
									(0·577 ± 0·080)	Hafemeister *et al.* (1964) (Area method)
									(0·613 ± 0·100)	(Line-width method)
	300°K	1·8163	2·0937	1·9742	1·9557	2·1175	2·0793	2·3633	2·2809	
				(1·73 ± 0·03)	(1·91 ± 0·07)	(1·98 ± 0·08)	(2·27 ± 0·04)	(2·19 ± 0·15)	(2·11 ± 0·16)	Beaver (1974)
				(1·79 ± 0·03)	(1·81 ± 0·08)					Barnea & Post (1966)

* B_K values shown here at 4·2°K have been derived using 80°K eigendata.

Theoretical results

In order to carry out the summation over $\mathbf{q}$ and j in equation (3) we use a sample of 64000 evenly spaced $\mathbf{q}$ vectors within the first Brillouin zone. Phonon frequencies and eigenvectors required in the summation were computed using two variations of the deformation dipole model. For model (1) the short-range repulsive forces are restricted to act only between nearest-neighbor unlike ions (Agrawal & Hardy, 1974), and for model (2) the short-range forces are extended to next nearest-neighbor ions and an angle bending force is introduced (Cunningham *et al.*, 1974).

The contribution of the region near the zone center ($\mathbf{q}\sim 0$) has to be evaluated separately, since the sum in equation (3) is singular at $\mathbf{q}=0$. However this singularity is integrable and we treat it by summing over a 'mini-zone' within the first Brillouin zone. This has the same shape as the first zone and has faces which contain the first points of the coarse mesh. The first mesh used to sum over this small region is ~ 1000 times denser than the coarse mesh. The resultant mean-square displacements and associated B_K values are given in Tables 1 and 2 and Table 3 respectively. At 300 and 80°K the contributions of the mini-zone to B_K have been found to be 3·5–4·0% for the rubidium halides and 2·2–2·5% for the cesium halides. At 4·2°K the corresponding contributions are much smaller and are 0·4–0·5% for the rubidium halides and 0·2–0·35% for the cesium halides. This appears to be in accord with the results obtained by Reid & Smith (1970) for NaCl.

Discussion

Our calculated values of $\langle U_K^2\rangle$ for the rubidium halides shown in Table 1 are consistent with the results of the shell-model calculations (Govindarajan, 1973) at 80°K; the difference between the two results is within 0·7–2·0% for all of the ions except for the Br^- and I^- ions where there is a difference of about 4%. The room-temperature values are not in such good agreement; the difference between the two model values is 8–11%. This is not surprising since both models give comparable fits to the 80°K dispersion curves but at 300°K there are so few experimental points that one cannot make the same statement. Consequently one may expect corresponding discrepancies between the eigendata generated by the two models. Calculated values of $\langle U_K^2 \rangle$ for the cesium halides are also shown in Table 2 but shell model results are not available for these crystals, thus no comparison is possible.

In Table 3 the computed B_K values are compared with the values derived from the measurements of the recoilless fraction for the Cs^+ ion in the cesium halides at 4·2°K and for the I^- ion in RbI and CsI at 80°K. The computed values of B_K for the I^- ion agree with the measured values within the experimental error. The computed and measured values for the Cs^+ ion are in agreement to within 3 or 4%. The experimental uncertainties are quoted as being less than 2% in all cases. It is possible that better agreement could be obtained for the Cs^+ ion if the eigendata used in this work were derived using 4·2°K input data in the lattice-dynamical calculations.

The calculated B_K values and those measured by X-ray diffraction for CsCl, CsBr, CsI, and RbCl at 300°K are also shown in Table 3. The computed and measured results agree within the experimental uncertainty for all the ions except for the Cl^- ion in RbCl, the Cs^+ ion in CsCl, and the Br^- ion in RbBr where the difference between the theoretical and experimental values is 10–12%. The computed room-temperature data should not be taken too seriously since no account has been taken of anharmonic effects. The experimental uncertainty in the X-ray measurements is also generally high.

In conclusion we can say that the computed results based on the DD models are generally in close agreement with the measured results. To obtain better agreement one should include anharmonic effects in the calculations. It would also be desirable to see measurements of B_K made as a function of temperature.

References

AGRAWAL, B. S. & HARDY, J. R. (1974). *Solid State Commun.* **14**, 239–244.

AGRAWAL, B. S. & HARDY, J. R. (1975). To be published.

BARNEA, Z. & POST, B. (1966). *Acta Cryst.* **21**, 181–182.

BEAVER, J. P. (1974). Ph. D. Thesis, Univ. of Nebraska, Lincoln. (Unpublished).

BOYLE, A. J. F. & PERLOW, G. J. (1966). *Phys. Rev.* **151**, 211–214.

CHIPMAN, D. R. & PASKIN, A. (1959). *J. Appl. Phys.* **30**, 1998–2001.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

CUNNINGHAM, S. L., SHARMA, T. P., JASWAL, S. S., HASS, M. & HARDY, J. R. (1974). *Phys. Rev.* B **10**, 3500-3511.

GOVINDARAJAN, J. (1973). *Acta Cryst.* A**29**, 576–577.

HAFEMEISTER, D. W., DE PASQUALI, G. & DE WAARD, H. (1964). *Phys. Rev.* **135**, B1089–B1101.

JAMES, R. W. (1965). *The Optical Principles of the Diffraction of X-rays*, p. 48. Ithaca: Cornell Univ. Press.

JARVINEN, M. & INKINEN, O. (1967). *Phys. Stat. Sol.* **21**, 127–135.

MARADUDIN, A. A., MONTROLL, E. W., WEISS, G. H. & IPATOVA, I. P. (1971). *Solid State Physics*, Suppl. 3, Chaps. 7 and 9. New York: Academic Press.

REID, J. S. & SMITH, T. (1970). *J. Phys. Chem. Solids*, **31**, 2689–2697.

Acta Cryst. (1975). A**31**, 252

A Probabilistic Theory in $P\bar{1}$ of the invariant $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$

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(*Received* 30 *October* 1974; *accepted* 2 *November* 1974)

Some joint probability distributions are studied in order to derive an estimate of the probability that the sign of the invariant $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ is positive. It is shown that this probability depends chiefly on the seven magnitudes $|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{l}}|, |E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|, |E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{h}+\mathbf{l}}|, |E_{\mathbf{k}+\mathbf{l}}|$, and may be larger as well as smaller than $\frac{1}{2}$.

Introduction

Schenk (1973*a*) has derived from semi-empirical observations a useful condition for strengthening the reliability of the relation

$$\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\simeq 0\,. \tag{1}$$

A weight E_4 which depends on $|E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{h}+\mathbf{l}}|, |E_{\mathbf{k}+\mathbf{l}}|$, was introduced for (1),

$$E_4=N^{-1}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|\left\{1+\frac{|E_{\mathbf{h}+\mathbf{k}}|+|E_{\mathbf{h}+\mathbf{l}}|+|E_{\mathbf{k}+\mathbf{l}}|}{E_{000}}\right\}. \tag{2}$$