

involved several assumptions in the evaluation of complicated lattice sums in reciprocal space, and, as the parameters are derived from the difference of terms in the potential energy, such discrepancies could easily arise. Detailed calculations in the manner of those made by Wolfe & Goodman (1969) would probably be required for each metal to give better agreement. Finally, it must be emphasized that the values obtained for the anharmonic term have been derived with the theoretical harmonic factors assumed to be correct and a 1% error in the latter would lead to a 15% error in the  $(m_e + m_{12})$  term.

### Conclusion

The application of the Mössbauer effect in the measurement of elastic Bragg scattering intensities free from inelastic phonon scattering contributions enables the Debye-Waller temperature factor to be found to sufficient accuracy to allow estimates of the amount of anharmonicity present in the atomic vibrations. The variation of the scattered intensities for a number of Bragg peaks was measured from 300 up to 900 K for aluminium and to 1200 K for copper single crystals and estimates of parameters arising from the non-Gaussian distribution of the thermal displacements at the higher temperatures were made and compared with theoretical estimates. The agreement with the general formulae derived by Maradudin & Flinn (1963) was poor, but values derived from the more sophisticated treatment used by Wolfe & Goodman (1969) were much closer.

*Acta Cryst.* (1978). **A34**, 505–512

## Anharmonic Contributions to Bragg Diffraction. II. Alkali Halides

BY C. J. MARTIN\* AND D. A. O'CONNOR

*Department of Physics, University of Birmingham, England*

(Received 12 September 1977; accepted 6 October 1977)

Anharmonic contributions to the atomic motion in the alkali halides KCl, NaCl, KBr and LiF have been determined from measurements of the elastic scattering of recoil-less  $\gamma$ -rays in the temperature range 300 to 1300 K. The results are compared with theoretical predictions.

\* Present address: Department of Medical Physics, University of Aberdeen, Scotland.

### References

- ALBANESE, G. & GHEZZI, C. (1973). *Phys. Rev. B*, **8**, 1315–1323.  
 BALDWIN, T. O. (1968). *Phys. Status Solidi*, **25**, 71–74.  
 BARRON, T. H. K., LEADBETTER, A. J., MORRISON, J. A. & SALTER, L. S. (1966). *Acta Cryst.* **20**, 125–131.  
 BUTT, N. M. & O'CONNOR, D. A. (1967). *Proc. Phys. Soc. London*, **90**, 247–252.  
 BUTT, N. M. & SOLT, G. (1971). *Acta Cryst.* **A27**, 238–243.  
 CHIPMAN, D. R. (1960). *J. Appl. Phys.* **31**, 2012–2015.  
 CHIPMAN, D. R. & PASKIN, A. (1959). *J. Appl. Phys.* **30**, 1992–1997.  
 DE MARCO, J. J. (1967). *Phil. Mag.* **15**, 483–495.  
 DINGLE, R. E. & MEDLIN, E. H. (1972). *Acta Cryst.* **A28**, 22–27.  
 FLINN, P. A., McMANUS, G. W. & RAYNE, J. A. (1961). *Phys. Rev.* **123**, 809–812.  
 GHEZZI, C., MERLINI, A. & PACE, S. (1969). *Nuovo Cimento B*, **64**, 103–116.  
 GILAT, C. & NICKLOW, R. M. (1966). *Phys. Rev.* **143**, 487–494.  
 LINKOAHO, M. V. (1971). *Philos. Mag.* **23**, 191–198.  
 McDONALD, D. L. (1967). *Acta Cryst.* **23**, 185–191.  
 MARADUDIN, A. D. & FLINN, P. A. (1963). *Phys. Rev.* **129**, 2529–2539.  
 NICKLOW, R. W. & YOUNG, R. A. (1966). *Phys. Rev.* **152**, 591–598.  
 O'CONNOR, D. A. (1967). *Proc. Phys. Soc. London*, **91**, 917–927.  
 O'CONNOR, D. A. & BUTT, N. M. (1963). *Phys. Lett.* **7**, 233–235.  
 OWEN, E. A. & WILLIAMS, R. W. (1947). *Proc. R. Soc. London, Ser. A*, **188**, 509–521.  
 WEBB, W. W. (1962). *J. Appl. Phys.* **33**, 3546–3552.  
 WOLFE, G. A. & GOODMAN, B. (1969). *Phys. Rev.* **178**, 1171–1189.

### Introduction

In the previous paper (Martin & O'Connor, 1978; referred to as paper I), the Mössbauer effect was used to separate the elastically and inelastically scattered components present in Bragg diffraction peaks in copper and aluminium, and from the temperature dependence of the elastic part calculations were made of the mean square atomic vibrational amplitudes. In the present work, similar measurements were carried out on the alkali halide crystals KCl, NaCl, KBr and LiF.

### Theory

The intensity of a Bragg diffraction peak  $I(\mathbf{Q})$  can be derived from a sum over the atomic scattering factors  $f_p$  including the appropriate phase factors,

$$I(\mathbf{Q}) = \left| \sum_p \sum_n f_{4p} \exp[i\mathbf{Q} \cdot (\mathbf{r}_n + \mathbf{r}_p + \mathbf{U}_p)] \right|^2, \quad (1)$$

where  $\mathbf{Q}$  is the scattering vector equal to the difference between the wave vectors of the incident and scattered  $\gamma$ -rays, and  $\mathbf{r}_p$  and  $\mathbf{U}_p$  represent the equilibrium position of the  $p$ th atom with respect to a primitive lattice point  $\mathbf{r}_n$  and its displacement from that position.

When applied to a diatomic molecule set in a cubic lattice the expression is simplified, for the reflections from the two types of atoms are either in phase (summation spectra) or out of phase (different spectra). The elastic intensities in the two cases are then given by:

$$I_{\text{SUM}} = E_p(\theta) |f_1 \exp(-W_1) + f_2 \exp(-W_2)|^2 \quad (2)$$

and

$$I_{\text{DIFF}} = E_p(\theta) |f_1 \exp(-W_1) - f_2 \exp(-W_2)|^2, \quad (3)$$

where the temperature dependence is expressed in terms of the Debye-Waller factor:

$$\begin{aligned} \exp(-W_p) &= \exp\left[-\frac{1}{2}\langle(\mathbf{Q} \cdot \mathbf{U}_p)^2\rangle\right] \\ &= \exp\left[-B_p \left(\frac{\sin \theta}{\lambda}\right)^2\right], \end{aligned} \quad (4)$$

where  $\theta$  is the Bragg angle,  $\lambda$  is the wavelength of the  $\gamma$ -rays,  $p(\theta)$  is an angle-dependent factor taking account of polarization and the volume of the crystal irradiated, and  $E$  is a constant intensity term. The scattering from the  $(nmn)$  planes in simple cubic alkali halide crystals depends on the sum of the scattering from the alkali and halide atoms if  $n$  is even, and the difference if  $n$  is odd.

If the intensities from the 222, 333 and 444 reflections are measured, the ratios  $I_{333}/I_{222}$  and  $I_{333}/I_{444}$  depend on the  $f$  values and the Debye-Waller factors. The separate Debye-Waller factors  $W_1$  and  $W_2$  can be found by varying them to fit both ratios. This method was used for the room-temperature results to provide

a check on the accuracy of the more convenient method which follows.

If values for intensities  $I_{\text{SUM}}$  and  $I_{\text{DIFF}}$  can be found for the same diffraction angle  $\theta$ , an expression for the structure factor ratios can be derived from (2) and (3), of the form:

$$\frac{\sqrt{I_{\text{SUM}}} + \sqrt{I_{\text{DIFF}}}}{\sqrt{I_{\text{SUM}}} - \sqrt{I_{\text{DIFF}}}} = \frac{f_1 \exp(-W_1)}{f_2 \exp(-W_2)}. \quad (5)$$

This gives a value for the difference in the Debye-Waller factors for the individual ions ( $W_1 - W_2$ ). If the intensity  $I_{\text{SUM}}$  is expressed in terms of a mean Debye-Waller factor  $\bar{W}$  defined by:

$$(f_1 + f_2)^2 \exp(-2\bar{W}) = |f_1 \exp(-W_1) + f_2 \exp(-W_2)|^2, \quad (6)$$

then  $W_1$  and  $W_2$  can be found from:

$$\exp[-(\bar{W} - W_2)] = \frac{f_2}{f_1 + f_2} \left[ \frac{f_1 \exp(-W_1)}{f_2 \exp(-W_2)} \right] + 1.$$

$I_{\text{DIFF}}$  was measured for the 333 plane and a value of  $I_{\text{SUM}}$  for the same diffraction angle estimated from the results for the even-order planes in the  $nmn$  series. The elastic intensity  $I_{\text{SUM}}$  can be written in the form:

$$I_{\text{SUM}} = E_p(\theta) (f_1 + f_2)^2 \exp\left[-2\bar{B} \left(\frac{\sin \theta}{\lambda}\right)^2\right]. \quad (7)$$

A graph of  $\ln\{I/(f_1 + f_2)^2 p(\theta)\}$  against  $(\sin \theta/\lambda)^2$  will thus be a straight line, and if the scattered intensities for the (222), (444) and (666) planes are measured, an estimate of  $I_{\text{SUM}}$  for the (333) planes at room temper-

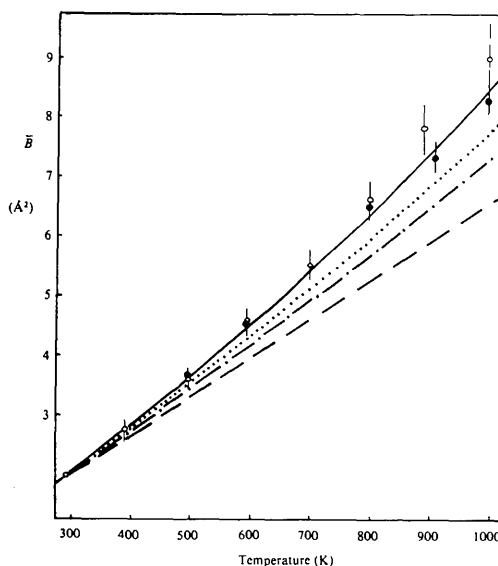


Fig. 1. Temperature dependence of the mean Debye-Waller factor for KCl. ● (400) plane results, ○ (600) plane results; — harmonic theory (Reid & Smith, 1970), - - - quasi-harmonic theory, — · — including additional  $T^2$  term, · · · · with  $T^3$  term found by including terms in  $T^3$ .

ature can be made from an extrapolation between them. The temperature dependence of the mean Debye–Waller factor was calculated from the (222) plane results, and this was then used to predict the temperature variation of  $I_{\text{SUM}}$  for the 333 plane. Some error is involved because the temperature factor in (4) was derived by assuming a Gaussian distribution of independent vibrations, which is no longer applicable at high temperatures, where

$$\exp(-W) = \exp\left\{-\frac{1}{2}\langle(\mathbf{Q}\cdot\mathbf{U})^2\rangle + \frac{1}{24}\langle(\mathbf{Q}\cdot\mathbf{U})^4\rangle - 3\langle(\mathbf{Q}\cdot\mathbf{U})^2\rangle^2\right\} \quad (8)$$

but the effect of the term in  $Q^4$  upon the values for  $I_{\text{SUM}}$  should be relatively small. The anharmonic terms were evaluated from the diffraction data for the  $n00$  planes, and the results were analysed in terms of the model developed by Willis (1969). He treated the crystals as Einstein solids with a potential for the  $p$ th atom of the form:

$$V_p(U_1 U_2 U_3) = V_0 + \frac{1}{2}\alpha_p U^2 + \beta_p U_1 U_2 U_3 + \gamma_p U^4 + \delta_p(U_1^4 + U_2^4 + U_3^4 - \frac{2}{3}U^4) \quad (9)$$

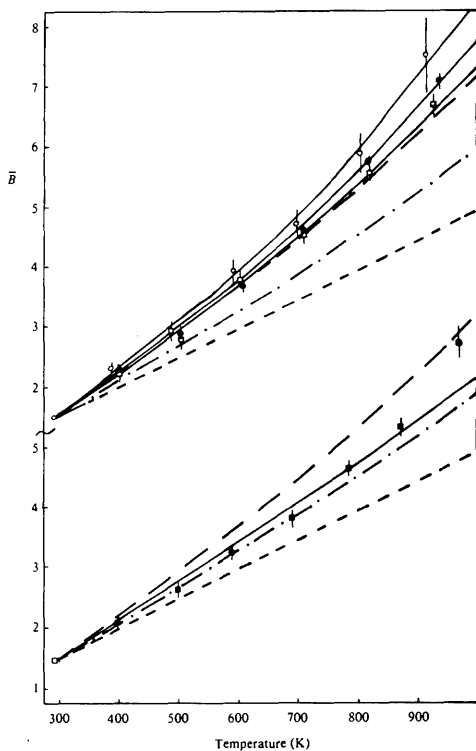


Fig. 2. Temperature dependence of the mean Debye–Waller factor for NaCl: ○ (600) plane results, ● (400) plane results, □ (200) plane results, ■ (222) plane results; - - - harmonic theory, - · - quasi-harmonic theory, — including terms in  $T^2$ , — including terms in  $T^3$  (non-Gaussian).

which yields an expression for the Debye–Waller factor of the form:

$$W_{Qp} = \frac{Q^2 KT}{2\alpha_p} + Q^2 (KT)^2 \left[ \frac{3\gamma_G(-2)\chi}{\alpha_p} - \frac{10\gamma_p}{\alpha_p^3} \right] - \frac{Q^4 (KT)^3}{\alpha_p} \gamma_p - \delta_p \left[ \frac{h^4 + k^4 + l^4}{(h^2 + k^2 + l^2)^2} - \frac{3}{5} \right] \quad (10)$$

where the Grüneisen parameter  $\gamma_G(-2)$  describing the volume dependence of the second moment of the frequency distribution and the thermal expansion coefficient  $\chi$  make up a term describing the volume dependence of  $W_{Qp}$ , and  $h, k, l$  are the Miller indices of the scattering plane. An additional term proportional to  $T^2$  contributes to the mean-square amplitude of the vibrations while the terms related to  $U^4$  in (8) are proportional to  $T^3$ . For ease of comparison with other results (10) was rewritten in the form

$$W_Q = \frac{Q^2 KT}{2\alpha_p} + (m_e + m_{12})(Qd)^2 \left(\frac{T}{\theta}\right)^2 + m_{34}(Qd)^4 \left(\frac{T}{\theta}\right)^3 \quad (11)$$

where  $d$  is the nearest-neighbour distance,  $m_e$  is the thermal expansion correction, and  $m_{12}$  and  $m_{34}$  are the anharmonic terms in  $\langle U^2 \rangle$  and  $\langle U^4 \rangle$ .

### Results and discussion

Crystals measuring  $2.0 \times 1.0 \times 0.2$  cm with faces parallel to the (100) and (111) planes were used for the experiments. These were lightly clamped to a stainless-steel plate within the furnace and annealed at about 50 K below their melting points until a fairly constant state of perfection had been reached before any measurements were taken.

For each crystal the temperature variations of the  $B$  factors (Figs. 1, 2, 3 and 4) were calculated from the scattering results after correcting for changes in the atomic scattering factor, the Lorentz–polarization factor and other expansion-sensitive terms. Estimates were made of the mean Debye–Waller factors at room temperature, and hence the mean Debye temperatures (Table 1) from fits of the results to the equation taking into account the effects of the thermal expansion term  $m_e$ , as described by (3) of paper I, with values for  $\gamma_G(-2)$  derived by Barron, Leadbetter & Morrison (1964) to describe the volume dependence of the second moment of the frequency distribution for NaCl and KCl, and values estimated from the results of Collins & White (1964) for KBr and LiF. The values for the mean Debye–Waller factors for KCl, NaCl and LiF agreed fairly well with other experimental determinations, but the results for KBr are slightly larger,

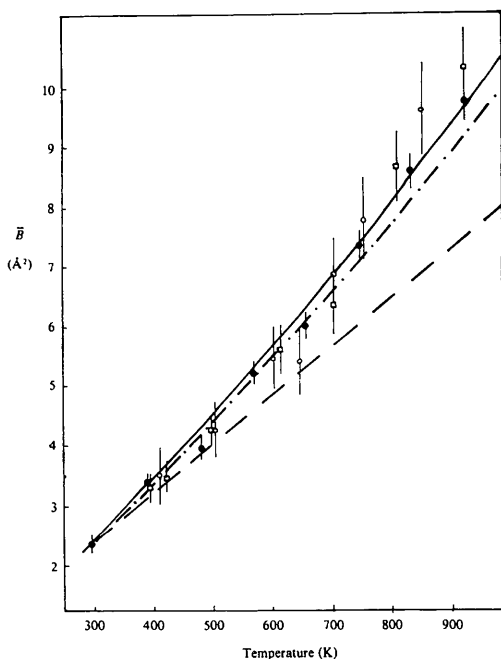


Fig. 3. Temperature dependence of the mean Debye-Waller factor for KBr: ○ (200) plane results, □ (400) plane results, ● (222) plane results; — harmonic theory, —·— quasi-harmonic theory, — fit with additional term in  $T^2$ .

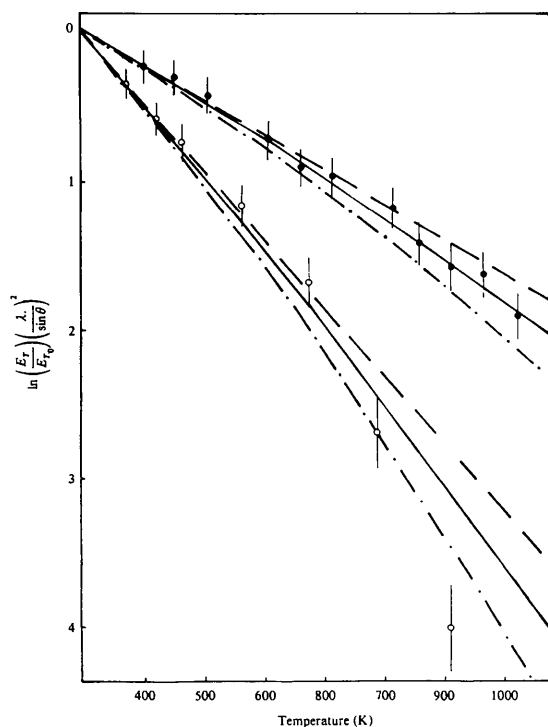


Fig. 4. Temperature dependence of the elastic scattering for LiF: ● (400) plane results; — harmonic theory, —·— quasi-harmonic theory, — fit including negative term in  $T^2$ .

possibly because of an undercorrection for the TDS in the X-ray experiments.

The Debye-Waller factors for the individual ions were computed from the mean values by comparing the (222) and (333) plane intensities. The differences between the factors, were, however, rather larger than other determinations, which have been made by measuring the integrated intensities for a large number of reflections from a crystal held at a fixed temperature. The results suggested that, as the melting temperature was approached the vibrational amplitude of the lighter alkali ions increased more than those of the halide ions (Figs. 5, 6 and 7), so the optical vibrations may increase near the melting point.

The intensity of scattering from all the planes in the  $h00$  series, where all the atoms scatter in phase, is of the  $I_{\text{SUM}}$  type in (2), so that only values for the mean Debye-Waller factors can be obtained. However, from the differences in the scattering curves for successive planes in the series, an estimate of the anharmonic contribution in  $U^4$  can be made with a similar technique to that described in paper I. Using (8) to compare the mean Debye-Waller factors for two sets of parallel planes described by  $Q_1$  and  $Q_2$ , at two temperatures  $T$  and  $T_0$ , Butt & Solt 1971 derived the expression

$$\frac{1}{(Q_1 d)^2 - (Q_2 d)^2} \left\{ \left[ \frac{2W_{Q_1}(T) - 2W_{Q_1}(T_0)}{(Q_1 d)^2} \right] - \left[ \frac{2W_{Q_2}(T) - 2W_{Q_2}(T_0)}{(Q_2 d)^2} \right] \right\} = D(T) - D(T_0)$$

where  $D(T) = (\langle U_Q^4 \rangle - 3\langle U_Q^2 \rangle^2)_T / d^4$ . This, written in terms of the measured intensities  $I_Q(T)$ , has the form:

$$D(T) - D(T_0) = \frac{1}{(Q_1 d)^2 - (Q_2 d)^2} \times \left[ \frac{1}{(Q_1 d)^2} \ln \left( \frac{I_{Q_1}(T_0)}{I_{Q_1}(T)} \right) - \frac{1}{(Q_2 d)^2} \ln \left( \frac{I_{Q_2}(T_0)}{I_{Q_2}(T)} \right) \right]$$

In the analysis  $T_0$  was taken as a reference temperature and the term  $D(T) - D(T_0)$  evaluated from differences in the curves depicting the temperature dependences of  $\{\ln[I_Q(T_0)/I_Q(T)]\}/(Qd)^2$  for different reflections, shown in Figs. 1 and 2 for KCl and NaCl. Plots of  $D(T) - D(T_0)$  against  $(T/H)^3$  (Figs. 8 and 9) confirmed the  $T^3$  dependence suggested by (11), and from the gradients the term  $m_{34}$  (Table 2) was calculated. The  $m_{34}$  parameters for NaCl and KCl were much smaller than those found experimentally by Butt & Solt (1971) and Solt, Butt & O'Connor (1973), but their results were taken over a limited temperature range and the scattering from the (200) plane, which could be badly

Table 1. *X-ray Debye temperature of the alkali halides at 300 K*

The symbols used to indicate the methods have the following meaning: Th theoretical, *X* X-ray,  $\gamma$   $\gamma$ -ray, *N* neutron, SC single crystal, *P* powder, *T* temperature dependence, *I* integrated intensity measurements.

Reference	Method	$B_+$ ( $\text{\AA}^2$ )	$B_-$ ( $\text{\AA}^2$ )	$\theta$ (K)
<b>KCl</b>				
Reid & Smith (1970)	Th	1.962	2.068	
Patomaki & Linkoaho (1969)	<i>X P I</i>	$2.08 \pm 0.05$	$2.06 \pm 0.05$	$213 \pm 8$
Viswamitra & Jayalakshmi Ramanuja (1972)	<i>X SC I</i>	$2.16 \pm 0.02$	$2.16 \pm 0.02$	$210 \pm 1$
Pathak & Trivedi (1973)	<i>X P T</i>			$220 \pm 3$
Albanese <i>et al.</i> (1973)	$\gamma$ SC <i>T</i>			$230 \pm 3$
Cooper & Rouse (1973)	<i>N SC I</i>	$2.175 \pm 0.007$	$2.165 \pm 0.007$	
Present results (400)	$\gamma$ SC <i>T</i>	$1.87 \pm 0.2$	$2.22 \pm 0.2$	$213 \pm 4$
(600)		$2.05 \pm 0.2$	$2.40 \pm 0.2$	$204 \pm 3$
After subtracting (400)		$1.72 \pm 0.2$	$2.07 \pm 0.2$	$218 \pm 4$
$T^3$ term (600)		$1.74 \pm 0.2$	$2.37 \pm 0.2$	$216 \pm 3$
Fit to $\exp(-W)$ (200)				$240 \pm 20$
<b>NaCl</b>				
Reid & Smith (1970)	Th	1.582	1.371	
Merisalo & Paakari (1967)	<i>X P I</i>	1.84	1.44	275
Linkoaho (1968)	<i>X P I</i>	$1.81 \pm 0.03$	$1.49 \pm 0.03$	274
Göttlicher (1968)	<i>X SC I</i>	1.89	1.61	265
Viswamitra & Jayalakshmi Ramanuja (1972)	<i>X SC T</i>	$1.59 \pm 0.08$	$1.37 \pm 0.05$	$286 \pm 3.5$
Butt <i>et al.</i> (1973)	<i>N P I</i>	$1.70 \pm 0.10$	$1.44 \pm 0.03$	
Present results (222)	$\gamma$ SC <i>T</i>	$1.98 \pm 0.1$	$1.26 \pm 0.1$	$281 \pm 4$
(200)		$2.16 \pm 0.1$	$1.44 \pm 0.1$	$266 \pm 4$
(400)		$2.12 \pm 0.1$	$1.40 \pm 0.1$	$269 \pm 4$
(600)		$2.48 \pm 0.15$	$1.70 \pm 0.1$	$244 \pm 6$
<b>KBr</b>				
Reid & Smith (1970)	Th	2.302	2.500	
Baldwin <i>et al.</i> (1965)	<i>X P T</i>			163
Pryor (1966)	<i>N SC I</i>	$2.20 \pm 0.10$	$2.28 \pm 0.10$	$161 \pm 4$
	<i>N P I</i>	$2.17 \pm 0.30$	$2.67 \pm 0.30$	$152 \pm 10$
Merisalo & Inkinen (1967)	<i>X P I</i>	$2.45 \pm 0.15$	$2.23 \pm 0.15$	$159 \pm 5$
Pathak & Trivedi (1973)	<i>X P Y</i>			$160 \pm 2$
Present results (222)	$\gamma$ SC <i>T</i>	$2.29 \pm 0.2$	$2.70 \pm 0.2$	$149 \pm 4$
(200)		$2.25 \pm 0.2$	$2.66 \pm 0.2$	$150 \pm 4$
(400)		$2.19 \pm 0.2$	$2.60 \pm 0.2$	$152 \pm 4$
(600)		$2.59 \pm 0.4$	$3.00 \pm 0.4$	$142 \pm 8$
<b>LiF</b>				
Pryor (1966)	Th	0.91	0.73	617
Witte & Wölfel (1958)	<i>X SC I</i>	1.10	0.67	614
Merisalo & Inkinen (1966)	<i>X P I</i>	$1.11 \pm 0.03$	$0.71 \pm 0.03$	613
Killeen <i>et al.</i> (1972)		0.96	0.66	
Howard & Khadake (1974)		$1.011 \pm 0.006$	$0.683 \pm 0.003$	
Present results (400)	$\gamma$ SC <i>T</i>	$1.675 \pm 0.3$	$0.50 \pm 0.2$	$630 \pm 8$
(600)		$1.672 \pm 0.3$	$0.53 \pm 0.2$	$616 \pm 20$

affected by extinction, was used. Moreover, the present values agree with theoretical values quoted in the above papers (Table 2). When the term in  $T^3$  was included in a fit of the data to (11) a closer approximation could be obtained for the temperature dependence, but still no account could be taken of the term  $m_{12}$  describing the anharmonic component of  $\langle U^2 \rangle$ . As the statistical errors in the scattering results were too large to determine the magnitude of both the  $T$  and  $T^2$  components from a computer fit of the data, it was decided instead to use theoretical values for the harmonic Debye-Waller factors and determine the component in  $T^2$  from a fit of the data, because a number of detailed calculations have been carried out for various harmonic

models. The data of Reid & Smith (1970) were chosen for the purpose, and this yielded a smaller value for the  $m_{12}$  parameter for KCl than had been found in previous experimental or theoretical treatments, suggesting that the  $m_{34}$  term might have been overestimated here, but the values for NaCl tallied reasonably well (Table 2). For KBr (Fig. 8) both terms are small, and indeed, the earlier X-ray results which give a smaller Debye-Waller factor make the  $m_{12}$  term negative. This is also the case for LiF, but the theoretical calculations of the harmonic factor used in this fitting are less sophisticated than those for the other materials. The measurements from the (400) plane of LiF (Fig. 9) demonstrate clearly the  $\exp(-W)$  temperature dependence caused by

extinction when compared with those of the  $\exp(-2W)$  type shown by the 600 reflection for the same crystal.

The formulation developed by Willis (1969) in (10) allows the coefficients  $\gamma$  and  $\delta$  in the potential equation to be calculated from a knowledge of  $m_{12}$  and  $m_{34}$ , and these are listed for the alkali halides studied in Table 3. The results for NaCl seemed to imply that the 222 plane had a much lower Debye-Waller factor than the  $n00$  planes. The  $m_{34}$  term, however, varies with crystallographic direction and since  $\gamma$  and  $\delta$  have been evaluated from the  $n00$  set of planes, the value of  $m_{34}$  can be predicted for the  $nnn$  set with (10). This showed

that the  $m_{34}$  term in fact made a negative contribution to  $W$  for the  $(nnn)$  planes, tying up the two sets of results surprisingly well (Fig. 2). Because of the approximate nature of the model, the result may be somewhat fortuitous; but it does supply strong evidence for the existence of quite large anharmonic contributions, which may account for some of the large discrepancies occurring in earlier NaCl measurements.

The variation in the magnitudes of the anharmonic terms in the different alkali halides allows no simple conclusions and implies that detailed theoretical

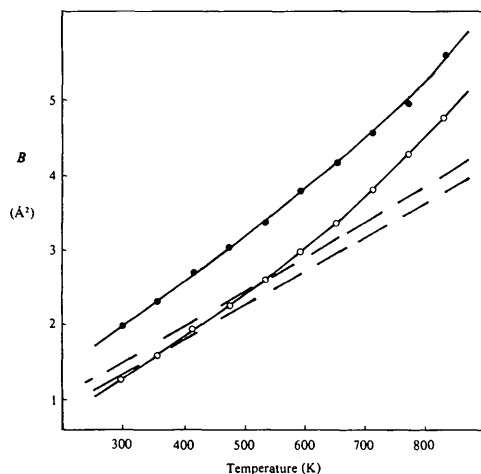


Fig. 5. Temperature variation of the Debye-Waller factors for the individual ions in NaCl: ●  $B_{\text{Na}^+}$ , ○  $B_{\text{Cl}^-}$ .

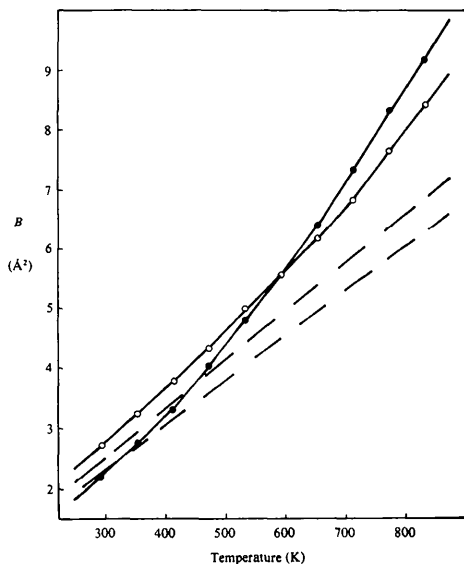


Fig. 6. Temperature variation of the Debye-Waller factors for the individual ions in KBr: ●  $B_{\text{K}^+}$ , ○  $B_{\text{Br}^-}$ ; — harmonic theory (Reid & Smith, 1970).

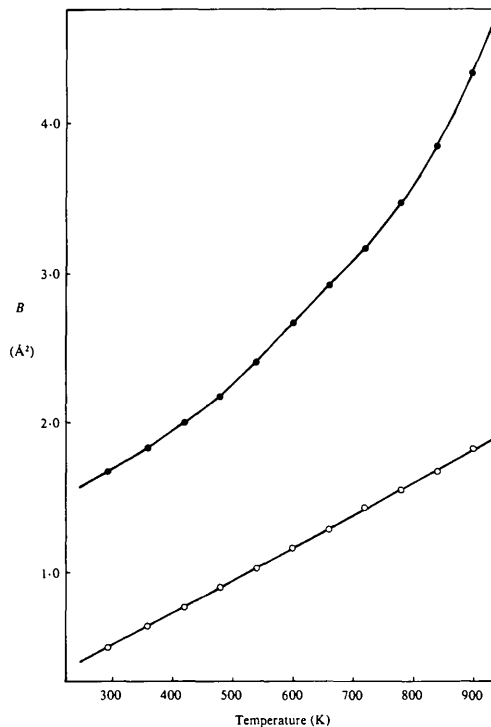


Fig. 7. Temperature variation of the Debye-Waller factors for the individual ions in LiF: ●  $B_{\text{Li}^+}$ , ○  $B_{\text{F}^-}$ .

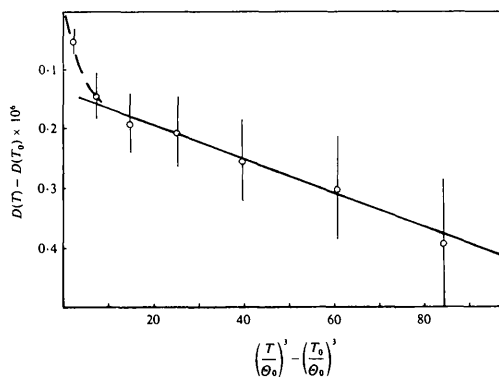


Fig. 8. The non-Gaussian contribution to the Debye-Waller factor for KCl.

Table 2. *Anharmonic Debye–Waller factor parameters for the alkali halides*

		Present results	Other experimental measurements	Anharmonic theory
KCl	$m_e + m_{12}$	$(0.79 \pm 0.04) \times 10^{-4}$		$0.39 \times 10^{-4a}$ $1.59 \times 10^{-4f}$
	$m_{12}$	$(0.40 \pm 0.04) \times 10^{-4}$	$0.79 \times 10^{-4b}$ $0.45 \times 10^{-4c}$ $0.79 \times 10^{-4d}$ $1.05 \times 10^{-4e}$	
	$m_{34}$	$(0.16 \pm 0.06) \times 10^{-4}$ including $T^3$ term $(3.0 \pm 1.0) \times 10^{-8}$ (400)/(600)	$(1.0 \pm 0.4) \times 10^{-6g}$	$2.58 \times 10^{-8g}$
NaCl	$m_e + m_{12}$	$(1.11 \pm 0.1) \times 10^{-4}$ (222) $(1.91 \pm 0.1) \times 10^{-4}$ (h00) $(0.12 \pm 0.1) \times 10^{-4}$ (222) $(0.92 \pm 0.1) \times 10^{-4}$ (h00)	$1.0 \times 10^{-4b}$ $1.77 \times 10^{-4c}$	$0.985 \times 10^{-4a}$ $2.88 \times 10^{-4f}$ $0.72 \times 10^{-4f}$
	$m_{34}$	$(4.1 \pm 1.0) \times 10^{-8}$ (200)/(400) $(5.8 \pm 1.0) \times 10^{-8}$ (400)/(600) $(5.2 \pm 1.0) \times 10^{-8}$ (200)/(600) $(5.0 \pm 0.5) \times 10^{-8}$ (Mean) $-18.6 \times 10^{-8}$ (222)	$2.4 \times 10^{-10h}$	$1.17 \times 10^{-7h}$
	$m_e + m_{12}$	$(0.49 \pm 0.03) \times 10^{-4}$	$0.208 \times 10^{-4i}$	$0.27 \times 10^{-4a}$ $0.91 \times 10^{-4f}$
	$m_{12}$	$(0.22 \pm 0.03) \times 10^{-4}$	$-0.139 \times 10^{-4j}$	$0.348 \times 10^{-4f}$ $0.418 \times 10^{-4k}$
	$m_{34}$	$(2.75 \pm 0.4) \times 10^{-4}$		$4.93 \times 10^{-4a}$ $11.242 \times 10^{-4f}$ $0.572 \times 10^{-4f}$
LiF	$m_e + m_{12}$	$(2.75 \pm 0.4) \times 10^{-4}$		$4.93 \times 10^{-4a}$ $11.242 \times 10^{-4f}$ $0.572 \times 10^{-4f}$
	$m_{12}$	$-(2.18 \pm 0.4) \times 10^{-4}$		
	$m_{34}$	$(2.3 \pm 1.0) \times 10^{-6}$ (400)/(600)		

References: (a) Quasi-harmonic theory. (b) Butt, Cheetham & Willis (1973). (c) Viswamitra & Jayalakshmi Ramanuja (1972). (d) Willis (1969) from results of James & Brindley. (e) Cooper & Rouse (1973) from measurements of scattering peaks at one temperature. (f) Kashiwase (1965). (g) Scott, Butt & O'Connor (1973). (h) Butt & Solt (1971). (i) Baldwin, Pearman & Tompson (1965). (j) Chandra, Prakash & Hemkar (1972) from Baldwin's results. (k) Cowley & Cowley (1966).

evaluations would have to be carried out for each one to give a reasonable picture. The general treatment used by Kashiwase (1965) yields terms of similar sign and magnitude for all the alkali halides. The fact that the terms are small and may be negative implies that the contributions from the cubic and quartic terms in the

Table 3. *Anharmonic coefficients of the potential energy derived from the model by Willis (1969)*

	$\alpha$ ( $\times 10^{12} \text{ \AA}^{-2}$ )	$\gamma$ ( $\times 10^{12} \text{ \AA}^{-4}$ )	$\delta$ ( $\times 10^{12} \text{ \AA}^{-4}$ )
KCl	1.64	$-0.19 \pm 0.02$	
KCl including $T^3$ term	1.64	$-0.08 \pm 0.03$	$1.4 \pm 0.4$
NaCl	2.24	$-0.51 \pm 0.06$	$1.8 \pm 0.6$
KBr	1.345	$-0.14 \pm 0.02$	$0.8 \pm 0.4$
LiF	4.10	$+0.83 \pm 0.15$	$1.4 \pm 0.6$

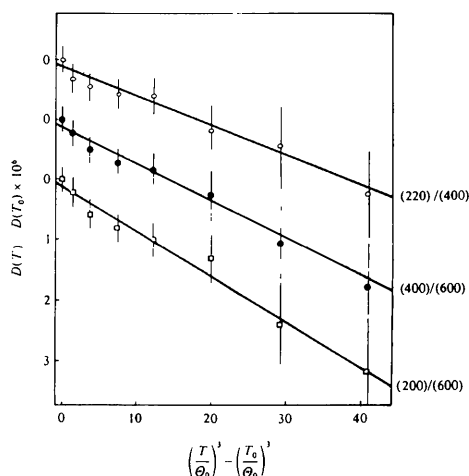


Fig. 9. The non-Gaussian contribution to the Debye–Waller factor for NaCl.

potential energy, which tend to cancel in the evaluations, may be finely balanced. Willis's (1969) model which uses an Einstein frequency distribution, avoids this cancellation at least in the  $T^2$  terms and the results suggest that the anisotropic  $U^4$  may be larger than the isotropic (Table 3).

### Conclusion

The application of the Mössbauer effect in separating the elastic scattering peaks from the TDS enables accurate measurements of the Debye–Waller factors to be made. The scattered intensities from a number of planes were measured for KCl, NaCl, KBr and LiF

from room temperature up to their melting points and from this, the vibrational amplitudes of the individual ions calculated and estimates made of parameters arising from the non-Gaussian distribution of the thermal displacements at high temperatures.

### References

- ALBANESE, G., GHEZZI, C. & MERLINI, A. (1973). *Phys. Rev. B*, **7**, 65–72.
- BALDWIN, T. O., PEARMAN, G. T. & TOMPSON, C. W. (1965). *J. Phys. Chem. Solids*, **26**, 303–306.
- BARRON, T. K. K., LEADBETTER, A. J. & MORRISON, J. A. (1964). *Proc. R. Soc. London, Ser. A*, **279**, 62–81.
- BUTT, N. M., CHEETHAM, A. K. & WILLIS, B. T. M. (1973). *Acta Cryst.* **A29**, 727–729.
- BUTT, N. M. & SOLT, G. (1971). *Acta Cryst.* **A27**, 238–243.
- CHANDRA, S., PRAKASH, J. & HEMKAR, M. P. (1972). *Indian J. Phys.* **46**, 579–585.
- COLLINS, J. G. & WHITE, G. K. (1964). *Prog. Low Temp. Phys.* **4**, 450–479.
- COOPER, M. J. & ROUSE, K. D. (1973). *Acta Cryst.* **A29**, 514–520.
- COWLEY, E. R. & COWLEY, R. A. (1966). *Proc. Phys. Soc. London, Sect. A*, **292**, 209–233.
- GÖTTLICHER, S. A. (1968). *Acta Cryst.* **B24**, 122–129.
- HOWARD, C. J. & KHADAKE, R. G. (1974). *Acta Cryst.* **A30**, 296.
- KASHIWASE, Y. (1965). *J. Phys. Soc. Jpn*, **20**, 320–335.
- KILLEAN, R. C. G., LAWRENCE, J. L. & SHARMA, V. C. (1972). *Acta Cryst.* **A28**, 405–407.
- LINKOAHO, M. V. (1968). *Ann. Acad. Sci. Fenn. Ser. A No.* **284**, pp. 1–31.
- MARTIN, C. J. & O'CONNOR, D. A. (1978). *Acta Cryst.* **A34**, 500–505.
- MERISALO, M. & INKINEN, O. (1966). *Ann. Acad. Sci. Fenn. Ser. A6*, No. pp. 207, pp. 1–24.
- MERISALO, V. & INKINEN, O. (1967). *Acta Cryst.* **22**, 58–65.
- MERISALO, M. & PAAKARI, T. (1967). *Acta Cryst.* **23**, 1107–1109.
- PATHAK, P. D. & TRIVEDI, J. M. (1973). *Acta Cryst.* **A29**, 477–479.
- PATOMAKI, L. H. & LINKOAHO, M. V. (1969). *Acta Cryst.* **A25**, 304–305.
- PRYOR, A. W. (1966). *Acta Cryst.* **20**, 138–140.
- REID, J. S. & SMITH, T. (1970). *J. Phys. Chem. Solids*, **31**, 2689–2697.
- SOLT, G., BUTT, N. M. & O'CONNOR, D. A. (1973). *Acta Cryst.* **A29**, 228–231.
- VISWAMITRA, M. A. & JAYALAKSHMI RAMANUJA, K. (1972). *Acta Cryst.* **A28**, S189–191.
- WILLIS, B. T. M. (1969). *Acta Cryst.* **A25**, 277–300.
- WITTE, H. & WÖLPEL, E. (1958). *Rev. Mod. Phys.* **30**, 51–55.

*Acta Cryst.* (1978). **A34**, 512–516

## Successive Refinement of Structures with Data of Increasing Resolution: A Theoretical Study for Triclinic Space Groups

BY S. PARTHASARATHY

*Molecular Biophysics Unit,\* Indian Institute of Science, Bangalore-560012, India and  
Department of Crystallography and Biophysics,† University of Madras, Guindy Campus, Madras-600 025, India*

(Received 4 August 1977; accepted 12 December 1977)

The method of least squares could be used to refine an imperfectly related trial structure by adoption of one of the following two procedures: (i) using all the observed at one time or (ii) successive refinement in stages with data of increasing resolution. While the former procedure is successful in the case of trial structures which are sufficiently accurate, only the latter has been found to be successful when the mean positional error (*i.e.*  $\langle |\Delta r| \rangle$ ) for the atoms in the trial structure is large. This paper makes a theoretical study of the variation of the *R* index, mean phase-angle error, *etc.* as a function of  $\langle |\Delta r| \rangle$  for data corresponding to different resolutions in order to find the best refinement procedure [*i.e.* (i) or (ii)] which could be successfully employed for refining trial structures in which  $\langle |\Delta r| \rangle$  has large, medium and low values. It is found that a trial structure for which the mean positional error is large could be refined only by the method of successive refinement with data of increasing resolution.

\* Communication No. 109.

† Contribution No. 470. Biophysics. For reprint requests use the Madras address.