profile of the 'defect' line becomes asymmetric and the 'defect' line turns into the 'excess-deficient' line as a result of anomalous absorption. The subsidiary maxima of Kikuchi lines, corresponding to the oscillation term in (4.5) are presented separately.

Calculated profiles of the Kikuchi band for reflexion 220 of a single Si crystal are plotted in Fig. 2. From these profiles it is clear that for an absorbing crystal, the band contrast is reversed at different thicknesses depending on the parameter $s=S(\mathbf{q}_0, \mathbf{q}_1)/S(\mathbf{q}_0, \mathbf{q}_0)$. Particularly for the thick crystal this is in accordance with the results of Okamoto *et al.* (1971) and Ishida (1971) and qualitatively explains the Kikuchi patterns observed by Shinohara *et al.* (1933), Boersch (1937), Pfister (1953) and Nakai (1970). Also, for a slightly absorbing crystal, when $\mu_h t \lesssim 1$ the band profile oscillates and the number (the amplitude) of oscillations varies directly (inversely) with the argument of w.

Conclusion

1. A consistent dynamical theory of Kikuchi patterns in two-beam approximation has been developed, which takes into account the absorption of both the elastically and inelastically scattered electrons in a crystal.
2. The formulae for calculation of the intensity profiles have been obtained.
3. The theory qualitatively explains the change of the Kikuchi patterns with increase in the crystal thickness.
4. As a result of anomalous absorption of inelastically scattered waves the 'defect' line becomes 'excess-deficient' in a thick crystal.
5. The oscillating term in the intensity distribution permits one to explain the fine structure of a Kikuchi pattern.
6. The method suggested in the present paper can be applied to the many-beam diffraction of inelastically scattered electrons in thick absorbing crystals.

References

Afanas'ev, A. M., Kagan, Yu. & Chukhovskii, F. N. (1968). *Phys. Stat. Sol.* **28**, 287–294.
Artmann, K. (1949). *Z. Phys.* **126**, 533–547.
Boersch, H. (1937). *Phys. Z.* **38**, 1000–1094.
Chukhovskii, F. N. (1968*a*). Thesis, Institute of Crystallography, Academy of Sciences of the USSR, Moscow.
Chukhovskii, F. N. (1968*b*). *Sov. Phys. Crystallogr.* **13**, 837–842.
Fues, E. & Riedel, H. (1949). *Ann. Phys.* **6**, 105–109.
Fujimoto, F. & Kainuma, Y. (1963). *J. Phys. Soc. Japan*, **18**, 1792–1804.
Hirsch, P. H., Howie, A., Nicholson, R. B., Pashley, D. W. & Whelan, M. J. (1965). *Electron Microscopy of Thin Crystals*. London: Butterworths.
Ichinokawa, T., Kamigaki, Y. & Ohtsuki, Y.-H. (1969). *Jap. J. Appl. Phys.* **8**, 969–970.
Ishida, K. (1970). *J. Phys. Soc. Japan*, **28**, 450–457.
Ishida, K. (1971). *J. Phys. Soc. Japan*, **30**, 1439–1448.
Kainuma, Y. (1955). *Acta Cryst.* **8**, 247–257.
Kikuchi, S. (1928). *Jap. J. Phys.* **5**, 83–96.
Lamla, E. (1938). *Ann. Phys. Leipz.* **32**, 178–189, 225–241.
Laue, M. von (1935). *Ann. Phys.* **23**, 705–746.
Laue, M. von (1948). *Materiewellen und ihre Interferenzen*, Leipzig: Akademische Verlag.
Meyer-Ehmsen, C. Z. (1969). *Z. Phys.* **218**, 352–377.
Nakai, Y. (1970). *Acta Cryst.* A**26**, 459–460.
Okamoto, K., Ichinokawa, T. & Ohtsuki, Y. H. (1971). *J. Phys. Soc. Japan*, **30**, 1690–1701.
Pfister, H. (1953). *Ann. Phys. Leipz.* **11**, 239–269.
Raether, H. A. (1962). *J. Phys. Soc. Japan, Suppl. B*-II, **17**, 61–68.
Shinohara, K. & Matsukawa, K. (1933). *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **21**, 21–25.
Takagi, S. (1958). *J. Phys. Soc. Japan*, **13**, 278–286, 287–296.
Watanabe, H. (1955). *J. Phys. Soc. Japan*, **10**, 908–909.

Acta Cryst. (1973). A**29**, 45

Debye Temperatures of KCl, KBr and RbCl by X-ray diffraction

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(*Received* 10 *April* 1972; *accepted* 24 *July* 1972)

Debye temperatures of KCl, KBr and RbCl have been determined by X-ray diffraction from room temperature up to about 800°K using methods due to Paskin [*Acta Cryst.* (1957). **10**, 667-669] and Chipman [*J. Appl. Phys.* (1960). **31**, 2012]. The anharmonic contribution to the Debye Θ is shown to come essentially from thermal expansion. The plot of the reduced thermal expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\theta^2$ gives a common curve for all the three halides. Here, $\alpha_{m/2}$ is the value of α at $T=\frac{1}{2}T_m$, T_m being the melting point, A is the mean atomic weight and a the lattice constant. An equation relating α, T and θ for the alkali halides is established for the first time. The values of the root mean square amplitudes, $(\overline{u^2})^{1/2}$, are calculated for the alkali halides from the equation and are compared with those of other workers.

Introduction

The temperature variations of the X-ray Debye temperatures of KCl and KBr have been investigated principally by Jaylakshmi & Viswamitra (KCl, 1970) and Baldwin, Pearman & Tompson (KBr, 1965). Reliable investigations on RbCl are not found in the literature.

Experimental

The experimental procedure is fully described by Pathak & Vasavada (1970). The profiles of lines 420 and 422 were recorded on a chart recorder and planimetered.

The accurate determination of the integrated intensity of a line profile of an X-ray reflexion depends, to some extent, on the proper estimation of the background. Normally, the background is estimated in two different ways: (i) a continuous curve is drawn touching the minima of the observed intensity distribution and (ii) the mean of the two minima adjacent to a given Bragg peak is taken to be the background for that peak. Both these methods are empirical and subjective, and subject to large systematic and random errors. Eastabrook & Wilson (1952), Tournarie (1956), Pike & Wilson (1959) and Langford & Wilson (1963) have discussed this aspect of the choice of the linear background. In the present investigation, the method used to determine the background was that given by Mitra & Misra (1966) who have studied the effect on different diffraction parameters of systematic errors arising from a wrong background level. The accuracy of the results is estimated at 1–2%.

Method of calculating Θ_M

(*a*) The most obvious method to obtain Θ_M would be to measure the intensities of several reflexions and to use the usual relation

$$\ln (f^2/F^2)=\ln K+2B\sin^2\theta/\lambda^2 \qquad (1)$$

where f is the atomic scattering factor, F the structure factor, B the Debye–Waller factor, θ the Bragg angle, λ the wavelength and K a constant. The plot of $\ln (f^2/F^2)$ *versus* $\sin^2\theta/\lambda^2$ will give both B, from the slope of the plot, and $\ln k$, from the intercept at $\sin^2\theta/\lambda^2=0$. The value of Θ_M is obtained from the measured value of B by using the Debye–Waller formula

$$2B=12h^2T\psi(x)/mk\Theta_M^2 \qquad (2)$$

where m is the mass of the atom, T the absolute temperature of the sample, $x=\Theta_M/T$ and

$$\psi(x)=\frac{1}{x}\int_0^x \frac{u\,du}{e^u-1}+\frac{x}{4}\,. \qquad (3)$$

$\psi(x)$ varies from 1·000 to 1·164 for $0\le x\le 2{\cdot}5$ and thus Equation (2) can be solved for Θ_M.

(*b*) After applying suitable corrections, equation (1) can be transformed into the following equation for a flat powder specimen of an f.c.c. crystal:

$$I=K'B'\exp\left[-\frac{12h^2}{mk}\cdot(1-\beta)\cdot\frac{\sin^2\theta}{\lambda^2}\cdot\frac{T\psi}{\Theta_M^2}\right] \qquad (4)$$

where I is the measured integrated intensity of a reflexion line, ψ is defined in equation (3), K' is a constant independent of Bragg angle and temperature T, B' is given by

$$B'=Npf^2\cdot\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}$$

where N is the number of unit cells irradiated and p is the multiplicity factor.

The quantity $(1-\beta)$ takes into account the one phonon thermal diffuse scattering (TDS) contribution

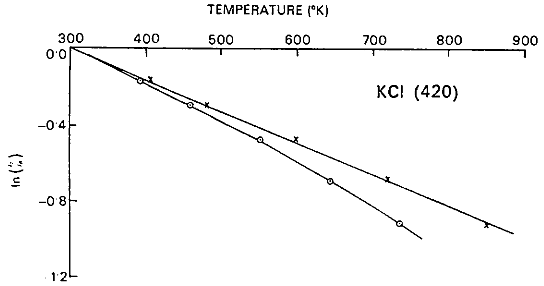

Fig. 1. Temperature dependence of the quantity $\ln I_T/I_R$ for the 420 reflexion of KCl. ○ $\ln I_T/I_R$ *versus* absolute temperature. × $\ln I_T/I_R$ *versus* reduced temperature.

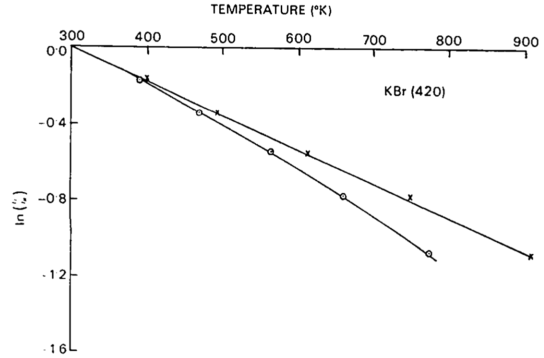

Fig. 2. Temperature dependence of the quantity $\ln I_T/I_R$ for the 420 reflexion of KBr. ○ $\ln I_T/I_R$ *versus* absolute temperature. × $\ln I_T/I_R$ *versus* reduced temperature.

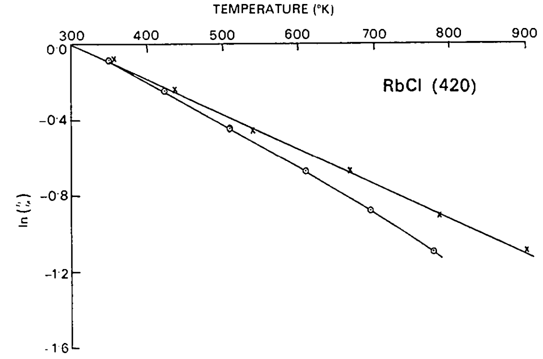

Fig. 3. Temperature dependence of the quantity $\ln I_T/I_R$ for the 420 reflexion of RbCl. ○ $\ln I_T/I_R$ *versus* absolute temperature. × $\ln I_T/I_R$ *versus* reduced temperature.

to the measured intensity according to Chipman & Paskin (1959). The quantity β for f.c.c. crystal is given by

$$\beta=\tfrac{1}{2}\left(\frac{\pi}{3}\right)^{1/3}\frac{a\cos\theta}{\lambda}\,.\,\Delta$$

where a is the lattice constant and Δ is the length of the straight-line background expressed in radians.

Writing equation (4) for temperatures T and T_0 and transforming we obtain

$$R=\frac{mk}{12h^2}\cdot\frac{\lambda^2}{(1-\beta)\sin\theta^2}\left[\ln\frac{I}{I_0}-\ln\frac{B'}{B'_0}\right]$$

$$=\frac{T_0\,\psi_0}{\Theta^2_{M0}}-\frac{T\,\psi}{\Theta^2_M}\cdot\frac{\sin^2\theta}{\sin^2\theta_0}\,. \quad (5)$$

T_0 may be any reference temperature, say room temperature. To calculate Θ_M from equation (5), either the value of Θ_{M0} is required or some additional relation between Θ_M and Θ_{M0} must be known. In the present investigation the following two additional relations have been used:-

(i) If the temperature dependence of Θ_M is due to volume expansion only, Θ_M can be obtained by using the relation $\Theta_M\{V(T)\}$. Zener & Bilinsky (1936), Owen & Williams (1947) and Paskin (1957) have discussed this aspect. According to Paskin

$$\theta_M/\theta_{M0}=(V_0/V)^{\gamma}$$

where V is the volume of the crystal at temperature T.

In practice, it is usually the thermal expansion that is measured. For isotropic cubic crystals, we therefore have

$$\Theta_M/\Theta_{M0}=(a_0/a)^{3\gamma} \quad (6)$$

where a is the lattice constant at temperature T. For $T\geq\Theta$, the Debye–Waller factor $2M$ is given by

$$2M=\frac{12\,h^2\sin^2\theta\,T}{mk\,\lambda^2\,\Theta^2_M}\,.$$

Substituting the value of Θ_M from equation (6) we obtain

$$2M=\frac{12\,h^2\sin^2\theta}{mk\lambda^2\,\Theta^2_{M0}}\left(\frac{a}{a_0}\right)^{6\gamma}T\,. \quad (7)$$

Thus $2M$ is seen to be proportional to the reduced temperature $T'=T(a/a_0)^{6\gamma}$. As the intensity I of a given line is proportional to exp $(-2M)$, it follows that

$$\ln\frac{I}{I_0}=-\frac{12h^2\sin^2\theta}{mk\,\lambda^2\,\Theta^2_{M0}}(T'-T'_0)\,. \quad (8)$$

Hence, if the temperature variation of Θ_M is really a volume effect, the plot of ln (I/I_0) *versus* T' must be a straight line.

From the slope of this line, the room temperature value of Θ *viz.* Θ_{M0} can be found. Θ_M can then be obtained from equation (5) for various temperatures.

(ii) Another way of estimating Θ_{M0} and hence Θ_M at various temperatures is that used by Chipman (1960). Using the fact that Θ *versus* T curves, as determined from the elastic constants, are approximately linear, one can plot a series of Θ *versus* T curves, giving Θ_0 a series of arbitrary values, and select the curve with smallest curvature.

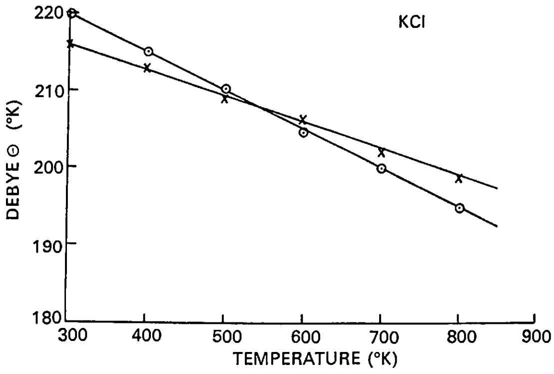

Fig. 4. The Debye Θ (average) *versus* temperature: –KCl. × Paskin's method, ○ Chipman's method.

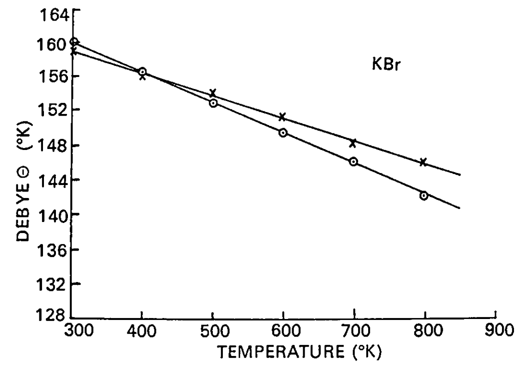

Fig. 5. The Debye Θ (average) *versus* temperature: –KBr. × Paskin's method, ○ Chipman's method.

Results and discussion

The plots of ln (I_T/I_R) (I_R = intensity at room temperature) *versus* reduced temperature $T'[T'=T(a_T/a_R)^{6\gamma}]$ for line 420 are given in Figs. 1, 2 and 3. Debye Θ_M at different temperatures are presented in Figs. 4, 5 and 6. The values of Θ_M in the plots are averages of those corresponding to the lines 420 and 422.

The room temperature values of Θ_M by Chipman's (1960) method are:

KCl = 220 ± 3 °K; KBr = 160 ± 2 °K;
RbCl = 156 ± 2 °K.

Since the plots of $\ln(I_T/I_R)$ *versus* reduced temperature (Figs. 1, 2, 3) are straight lines, it is evident that the anharmonic contribution to the Debye Θ in the range of temperatures examined comes essentially from thermal expansion.

Cartz (1955) has considered the temperature variation of thermal diffuse X-ray scattering and has shown that the amplitude of thermal vibrations of atoms in cubic crystals can be expressed in terms of the distance between neighbouring atomic positions and the melting point. He has also shown that a 'law of corresponding states' exists in the case of physical properties like thermal expansion, Debye Θ *etc.* which depend on atomic vibrations.

The common relation given by him between thermal expansion and the mean square amplitude of atomic vibrations, $\overline{u^2}$, for all *cubic metals* is

$$\alpha/\alpha_{m/2} = 0{\cdot}74 + 10{\cdot}7\ (\overline{u^2}/r^2) \qquad (9)$$

where $\alpha_{m/2}$ is the coefficient of thermal expansion at $T=\frac{1}{2}T_m$ (T_m being the melting point) and r is half the distance between neighbouring atomic positions. Since, for $T > \Theta$,

$$\overline{u^2} = \frac{9h^2T}{4\pi^2 mk\Theta^2} = 4{\cdot}364 \times 10^{-14}\frac{T}{A\Theta^2} \qquad (10)$$

we have

$$\alpha/\alpha_{m/2} = 0{\cdot}74 + 0{\cdot}374 \times 10^{-11}\ T/Aa^2\ \Theta^2 \qquad (11)$$

where a is the lattice parameter given by $r = a/2\sqrt{2}$ for the f.c.c. structure.

In view of the present accurate determinations, it was thought to be of interest to draw the curve between $\alpha/\alpha_{m/2}$ and $T/Aa^2\Theta^2$ and to see if the law of corresponding states holds for *alkali halides*. The curve is shown in Fig. 7 and is given by

$$\alpha/\alpha_{m/2} = 0{\cdot}70 + 0{\cdot}364 \times 10^{-11}\ T/Aa^2\Theta^2 \qquad (12)$$

The root mean square amplitudes of atomic vibrations, $(\overline{u^2})^{1/2}$, obtained using equation (12) are given in Table 1 and compared with those of other workers. The estimated error in $(\overline{u^2})^{1/2}$ is about 8%. Since the values of the root mean square amplitudes of all the halides obtained from equation (12) agree well with those of other workers, it is reasonable to assume that this equation is common to all the alkali halides.

Table 1. *Root mean square amplitudes of atomic vibrations at room temperatures*

NaCl type	From Equation (12)	$(\overline{u^2})^{1/2}$ Lonsdale (1948)	$(\overline{u^2})^{1/2}$ Linkoaho (1969)
KCl	0·27	0·26	0·28
KBr	0·29	0·27	0·29
KI	0·31	0·30	0·34*
KF	0·21	0·21	
NaCl	0·23	0·24	0·24
NaBr	0·25	0·25	
NaI	0·26	0·28	
NaF	0·17	0·19	0·20
RbCl	0·29	0·26	0·29
RbBr	0·31	0·29	
RbI	0·34	0·32	
LiF	0·16		0·17
LiCl	0·24		0·22

* Pearman & Tompson (1967).

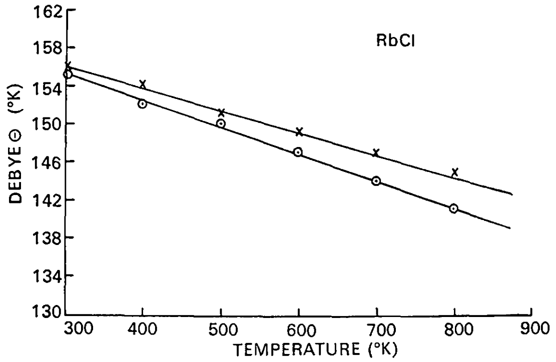

Fig. 6. The Debye Θ (average) *versus* temperature: –RbCl. × Paskin's method, ○ Chipman's method.

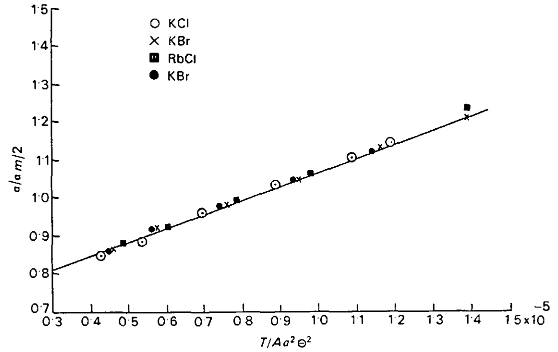

Fig. 7. Plot of reduced expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\Theta^2$. a is the lattice parameter, A mean atomic weight, Θ Debye temperature and $\alpha_{m/2}$ is the value of α at $T=\frac{1}{2}T_m$. ● KBr, Baldwin *et al.* (1965); × KBr, ○ KCl, ■ RbCl, present paper.

The values of Θ used to draw Fig. 7 were those determined by Chipman's method. The values of α for KCl were obtained from Pathak & Vasavada (1970) while those for RbCl were communicated by Dr Vasavada prior to publication. Values of α for KBr (to be published separately) were determined by the authors. Further work on other alkali halides is in progress.

Financial assistance to one of us (JMT) by the Gujarat University is gratefully acknowledged.

References

Baldwin, T. O., Pearman, G. T. & Tompson, C. W. (1965). *J. Phys. Chem. Solids*, **26**, 303–306.

Cartz, L. (1955). *Proc. Phys. Soc.* B**68**, 957–967.

Chipman, D. R. (1960). *J. Appl. Phys.* **31**, 2012–2015.

Chipman, D. R. & Paskin, A. (1959). *J. Appl. Phys.* **30**, 1992–1997, 1998–2001.

Eastabrook, J. N. & Wilson, A. J. C. (1952). *Proc. Phys. Soc.* B**65**, 67–75.

Jaylakshmi, K. & Viswamitra, M. A. (1970). *Proc. Nucl. Phys. Solid State Phys. Symp. Madurai, India.* Vol. III, p. 373.

LANGFORD, J. I. & WILSON, A. J. C. (1963). *Crystallography and Crystal Perfection*. Edited by G. N. RAMACHANDRAN, p. 207. London: Academic Press.
LINKOAHO, M. V. (1969). *Acta Cryst.* A**25**, 450–459.
LONSDALE, K. (1948). *Acta Cryst.* **1**, 142–149.
MITRA, G. B. & MISRA, N. K. (1966). *Br. J. Appl. Phys.* **17**, 1319–1328.
OWEN, E. A. & WILLIAMS, R. W. (1947). *Proc. Roy. Soc.* A**188**, 509–521.
PASKIN, A. (1957). *Acta Cryst.* **10**, 667–669.
PATHAK, P. D. & VASAVADA, N. G. (1970). *Acta Cryst.* A**26**, 655–658.
PEARMAN, G. T. & TOMPSON, C. W. (1967). *J. Phys. Chem. Solids*, **28**, 261–266.
PIKE, E. R. & WILSON, A. J. C. (1959). *Br. J. Appl. Phys.* **10**, 57–68.
TOURNARIE, M. (1956). *C.R. Acad. Sci. Paris*, **242**, 2161–2164.
ZENER, C. & BILINSKY, S. (1936). *Phys. Rev.* **50**, 101–104.

Acta Cryst. (1973). A**29**, 49

A Neutron-Diffraction Study of ZnS and ZnTe

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(*Received* 22 *March* 1972; *accepted* 17 *August* 1972)

Accurate integrated intensities for the Bragg reflexion of neutrons by crystals of ZnS and ZnTe have been measured at room temperature. Measurements were made at a number of wavelengths and corrections were made for extinction and thermal diffuse scattering. The experimental data show contributions arising from third-order anharmonic thermal vibration of the ions. However, it is shown that, although both types of ion have a tetrahedral site symmetry and can thus give rise to such anharmonic contributions, only a single anharmonicity parameter can be determined from the neutron measurements. The magnitude of the anharmonicity parameter is similar to that obtained for the fluorine ions in CaF_2, SrF_2 and BaF_2. The nuclear scattering amplitude of zinc was refined to $b_{Zn}=0{\cdot}569(2)\times10^{-12}$ cm, assuming a value for the nuclear scattering amplitude of sulphur of $b_S=0{\cdot}2847(1)\times10^{-12}$ cm.

Introduction

In almost all cases determination of crystal structures is carried out using models which assume harmonic thermal vibration for all constituent atoms. The thermal vibration of each atom is thus constrained such that the time averaged probability function for the position of an atom is a Gaussian function of the displacement from its equilibrium position and contours of equal probability are ellipsoids. However, in a crystal the nearest neighbours will be arranged necessarily with a particular symmetry which one would expect to influence the thermal vibration of the atoms. For example, in a cubic crystal such as CaF_2 or ZnS, with atoms having neighbours situated at the corners of a tetrahedron, it is reasonable to expect the thermal vibration to be distorted from the harmonic cubic (spherical) symmetry by a contribution such that the atoms spend more time in directions away from the nearest neighbours than in directions towards them, *i.e.* the thermal vibration includes an anharmonic component with tetrahedral symmetry. Such anharmonic components will contribute to the diffracted Bragg intensities and can be readily observed in such structures as the fluorite structure, *e.g.* in BaF_2 contributions of about 10% have been observed in room temperature neutron-diffraction measurements. Thus careful diffraction measurements can give valuable information about the thermal vibration of the atoms and the effect on this of the site symmetry.

In earlier papers we have described series of accurate intensity measurements for the Bragg reflexion of neutrons from BaF_2 (Cooper, Rouse & Willis, 1968) and SrF_2 and CaF_2 (Cooper & Rouse, 1971). These materials all have the cubic fluorite structure and the neutron data were found to show significant effects arising from a third-order anharmonic component in the thermal vibration of the fluorine ions, as allowed by their non-centrosymmetric site symmetry. These earlier measurements thus confirmed the importance of anharmonic effects for atoms occupying tetrahedral sites in the fluorite structure and further measurements have now been carried out in order to explore the possible importance of anharmonic effects in other types of structure. The present paper describes measurements which have been made on crystals of ZnS and ZnTe.

Considerable care was exercised in these measurements in order to achieve data which were considered to be reliable to the required level of accuracy. The