and assume this motion to be equal to the average mean-square displacement of the adjacent atoms A and B. This leads to $T_{jis}=(T_{js}+T_{is})/2$ and implies that no phase relationship exists between the displacements of atoms A and B. As the thermal motion is generally an average over many external and internal modes, this assumption is not unreasonable.

The assignment of the single parameter T_{jis} to the whole overlap density implies that the thermal motion varies little in the region of the bond, *i.e.* that $T_{js} \sim T_{is}$. A better approximation to (21) is to be used if this condition is not fulfilled.

Conclusion

We have outlined formalisms and practical considerations pertinent to the population refinement of X-ray diffraction data. This refinement can produce detailed information on the molecular charge-distribution. But, because large correlations exist between its elements, the first-order density matrix cannot be fully determined experimentally, even when 'long bonds' are neglected. The treatment of thermal motion is approximate, and further studies on the effect of thermal averaging are desirable.

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Structure Factor Amplitudes from Thermal Diffuse Scattering Measurements

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A method is proposed, for certain single crystals, of estimating the structure factor amplitudes corresponding to Bragg reflexions with strong to medium integrated intensities from measurements of the thermal diffuse X-ray scattering in regions of reciprocal space close to the appropriate lattice points. The values obtained conventionally from integrated Bragg intensities are often subject to considerable error due to extinction effects. The thermal diffuse scattering, being incoherently scattered and of a relatively weak intensity, would appear to be less likely to be affected by primary and secondary extinction. The structure factor amplitudes (or correction factors for those found from Bragg measurements) are obtained from the observed scattering data by a least-squares refinement method. Procedures are suggested for use where measurements are made on (i) a relative scale, (ii) an absolute scale, with respect to the direct beam intensity. The method is illustrated by application to some single-crystal data.

Introduction

In recent years, considerable progress has been achieved in providing estimates of extinction effects in the determination of structure factor amplitudes from integrated Bragg intensities, by both experimental (Chandrasekhar, Ramaseshan & Singh, 1969) and theoretical (Zachariasen, 1967, 1968*a*,*b*,*c*,*d*, 1969; Coppens &

Hamilton, 1970) methods. The importance of the effects depends on the crystalline state of the sample. The result is an attenuation of the diffracted beam intensity, usually being of greater significance for strong to medium intensity reflexions. However, it is in regions of reciprocal space close to such points that the thermal diffuse scattering is of sufficient intensity to permit reasonably reliable measurement. The thermal diffuse scattering, being incoherent and of relatively weak intensity, would appear to be less likely to be affected by extinction. Procedures for the determination of its effects are considered in the following sections.

A summary of the expressions used in the refinement procedures

The general expressions for the integrated Bragg intensity and the intensity of thermal diffuse scattering (neglecting higher than second order photon–phonon interactions) from a single crystal are:

(i) *Bragg scattering (assuming an ideally mosaic single crystal)*

$$\frac{E\omega}{I_0} = \left(\frac{e^2}{mc^2}\right)^2 p \frac{L}{\tau^2} |F_B|^2 A(\mu)\, \Delta v\dagger \qquad (1)$$

(*International Tables for X-ray Crystallography*, 1962).

(ii) *Thermal diffuse X-ray scattering*

$$I'_d(\text{obs}) = I_o\left(\frac{e^2}{mc^2}\right)^2 \frac{p\Omega q^2kT}{\tau^2} A(\mu)\Delta v$$
$$\times \left[|F_D|^2K[ABC]_{hkl} \cdot \frac{1}{R^2} + \frac{\pi^3}{2} kTq^2|F_D|^2 \times K'[ABC]_{hkl} \cdot \frac{1}{R} + \cdots\right] \qquad (2)$$

(Ramachandran & Wooster, 1951). Combining these equations and introducing the requirement for the least-squares refinement method, leads to the condition that the following expression

$$\sum_i \left[GH\alpha^2K'[ABC]_{hkl} \cdot \frac{1}{R_i} + G\alpha^2K[ABC]_{hkl} \cdot \frac{1}{R_i^2} - I'_{d_i}(\text{obs})\right]^2 \qquad (3)$$

(Lucas, 1968, 1970) should be a minimum. Expressions for the constants used in equation (3) are shown in Table 1.

$$K[ABC]_{hkl} = \sum_{\alpha=1}^{3} \frac{\cos^2(q, \xi_\alpha)}{\delta \,.\, V_\alpha^2}$$

and $K'\ [ABC]_{hkl} = \sum_{\alpha=1}^{3} \frac{\cos^4(q, \xi_\alpha)}{\delta^2 \,.\, V_\alpha^4}$

$$H = \frac{\pi^3}{2} kTq^2 \,.$$

Table 1. *Expressions for the constants used in equation* (3)

	$A(\mu)\Delta v$	Absolute scale α	Absolute scale G	Relative scale α	Relative scale G
Crystal element	(Δv, if absorption may be neglected)	$\lvert F_D\rvert$	$U \,.\, A(\mu)\Delta v$	$\frac{\lvert F_D\rvert}{\lvert F_B\rvert}$	W
Crystal face	$\frac{1}{2\mu}$				

where

$$U = I_0\left(\frac{e^2}{mc^2}\right)^2 \frac{p}{\tau^2} (q^2\Omega kT) \text{ and } W = \frac{E\omega}{L\lambda^3} (q^2\Omega kT) \,.$$

The measurements of the thermal diffuse scattering intensity may either be made on an 'absolute scale' when I_0 and $A(\mu)\Delta v$ are required, or on a 'relative scale' when the usually more accessible quantity, E, is required.

Results

For illustration, the method was applied to the experimental data obtained by Ramachandran & Wooster (1951) for KCl. Examples of the rate of convergence are given in Table 2. Values found for different sets of measurements are shown in Table 3.

Table 2. *Example of convergence rate*

Reciprocal lattice point, *hkl*		400	440
$[ABC]$	Cycle	$\lvert F_D\rvert$	$\lvert F_D\rvert$
[110]	(initial value)	50·00	50·00
	1	63·39	43·55
	2	62·09	43·00
	3	62·07	42·99
	4	62·07	42·99

Table 3. $\lvert F_D\rvert$*-values from various sets of data*

hkl	$[ABC]$	$\lvert F_D\rvert$	$\lvert F_C\rvert$
400	[100]	61·93	67·15
	[110]	62·07	
440	[010]	40·02	45·18
	[111]	43·03	
	[110]	42·99	

[$\lvert F_C\rvert$-values were obtained from the calculated Dirac–Slater atomic scattering factors of Cromer & Waber (1965) and the thermal parameters given by Wasastjerna (1946)].

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† The meanings of symbols are given in the Appendix.

Concluding remarks

The use of equation (2) to represent adequately the thermal diffuse scattering intensity (assumed equal to the diffuse intensity remaining after various contributions, *e.g.* Compton, instrumental, and air scattering *etc.*, have been subtracted from the total diffuse intensity in regions close to reciprocal-lattice points) has been shown only for cubic and a few other lower symmetry single crystals of an atomic rather than molecular nature (Wooster, 1962). However, it would appear that for certain crystalline materials, the method outlined above offers an experimental procedure for structure factor amplitude estimate (or correction) which is additional to, and independent of, the conventional method based on integrated Bragg intensity measurements. This information is derived from experimental data which are normally neglected.

For different experimental-measurement procedures and different sample crystal sizes and shapes, the common form of the least-squares refinement condition [equation (3)] is convenient, because of the versatility of the computer program. Automatic (or semi-automatic) diffractometers could have additional setting instructions introduced to make the required stationary measurements, close to the lattice points, of thermal diffuse scattering with strong to medium integrated Bragg intensities. The refinement procedure could be incorporated in the data reduction program to obtain either corresponding structure factor amplitudes on an absolute scale or a correction factor by which the structure factor amplitudes obtained from integrated Bragg intensities should be scaled to normalize them to the weaker (assumed less affected) intensities.

The method described permits cross-checks on the $|F|$-values obtained by making thermal diffuse scattering measurements along different directions, $[ABC]$, close to each lattice point. The results of the refinement, which were used to illustrate the method, show a quite rapid convergence and yield values for the structure factor amplitudes with reasonable consistency between values obtained by measurements of the thermal diffuse scattering along different directions and differ by $\sim$4 to 7% from the calculated values. [Some uncertainties remain, however, in the general calculations of structure factor amplitudes from calculated atomic scattering factors and these could be as large as $\sim$3% – see, for example Coppens (1969).]

APPENDIX

Table of symbols

$A(\mu)$	Absorption correction, $(\Delta v)^{-1}\int_{\Delta v}\exp(-\mu[T_1+T_2])\mathrm{d}\tau$
A,B,C	Directional indices
c	Velocity of light
e	Electronic charge
E	Total energy diffracted
$\lvert F_B\rvert$	Structure amplitude (at temperature T) from integrated Bragg intensity measurement
$\lvert F_D\rvert$	Structure amplitude (at temperature T) from thermal diffuse scattering measurements
$\lvert F_C\rvert$	Calculated structure amplitude (at temperature T)
G	Appropriate expressions, involving combinations of certain symbols included here, are given in Table 1.
h,k,l	Miller indices
$I'_d(\text{obs})$	Total diffuse intensity observed at a point in reciprocal space, less background
$I'_{d_i}(\text{obs})$	Value of $I'_d(\text{obs})$, for the ith measurement
I_o	Intensity per unit area of cross-section of the direct beam
k	Boltzmann constant
L	Lorentz-factor ($=1/\sin 2\theta$)
m	Mass of the electron
p	Polarization factor
q	Distance of the reciprocal-lattice point to the origin
R	Distance from the point of diffuse scattering observation to the nearest reciprocal-lattice point
R_i	Value of R, for the ith measurement
T	Absolute temperature
T_1	Path length of the incident beam direction in the entire crystal
T_2	Path length of the diffracted beam direction in the entire crystal
V_α, $(\alpha=1,2,3)$,	Velocities of the three acoustical waves having the wave vector $\mathbf{R}$
Δv	Volume of the crystal
α	Appropriate expressions, involving combinations of certain symbols included here, are given in Table 1.
δ	Crystal density
θ	Bragg angle
λ	Wavelength of radiation
μ	Linear absorption coefficient
ξ_α, $(\alpha=1,2,3)$,	Amplitudes of the three acoustical waves having the wave vector $\mathbf{R}$
τ	Volume of unit cell
ω	Uniform angular velocity of rotation of the crystal
Ω	Solid angle subtended by the detector at the crystal

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Structure and Growth of Three New Polytypes of Cadmium Iodide 60*R*, 72*R*, and 32*H*. A New Possible Method of Determining Atomic Structure of Polytypes Based on Evaluation of Theoretical Stacking Fault Energy

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Three new polytypes of cadmium iodide, two rhombohedral 60*R* and 72*R* and one hexagonal 32*H* have been discovered. The detailed atomic structures of 60*R* and 72*R* have been worked out; these are $[(22)_3\ 1223]_3$ and $[(22)_4\ 1223]_3$. These structures indicate the existence of a structure series $[(22)_n\ 1223]_3$. The growth of the polytypes 60*R* and 72*R* has been discussed in terms of creation of periodic stacking faults in the basic structure. Evidences and arguments including electron microscope observations of dislocation dissociation have been presented to show that the proposed mechanism is the most likely one through which the above polytypes have resulted. Following Hirth & Lothe, theoretical stacking fault energies of the probable structures of the two polytypes have been calculated and it has been found that the stacking fault energies for the proposed structures are minimum. Based on this criterion the structure of 32*H* was deduced and was found to represent the correct atomic structure. It seems possible that the minimum stacking fault energy criterion may prove to be of value in general in determining the atomic structure of polytypes.

Introduction

Cadmium iodide is a curious compound since it is known to exist in more than one hundred polytypic modifications (Srivastava & Verma, 1965; Chadha & Trigunayat, 1967). However, only two of these crystallographic modifications have been shown to be rhombohedral (Chadha & Trigunayat, 1967). The rhombohedral cadmium iodide polytypes present a very interesting feature since, unlike rhombohedral polytypes of other substances, these do not seem to result from any of the basic structures (Srivastava & Verma, 1965). Recently it has been suggested that these polytypes may form as a result of layer transpositions and creation of stacking faults (Chadha & Trigunayat, 1967). However, no evidence has been presented to show that a complex sequence of basal stacking faults can occur in cadmium iodide structures. The existence of the polytypes 60*R* and 72*R* suggests the occurrence of a structural series represented by the Zhdanov symbol $[(22)_n1223]_3$ in cadmium iodide polytypes. The scheme through which stacking faults could generate 60*R*, 72*R* polytypes has been described and discussed. Electron microscope observation which present evidence in favour of suggested mechanism has been presented. In order to test whether a polytypic structure corresponds to minimum stacking fault energy, which it should in principle if it has resulted from a basic structure through the occurrence of a stacking fault, theoretical stacking fault energies for the polytypes 60*R* and 72*R* were calculated. It was found that the atomic structure calculated, based on X-ray diffraction intensities, represented the atomic sequence with minimum stacking, fault energies. This procedure applied in the reverse way resulted in the determination of correct atomic structure for the polytype 32*H*.

Observation and results

The crystals were grown from aqueous solution and were investigated by X-ray diffraction single-crystal oscillation and Weissenberg photographs. The polytypes 60*R* and 72*R* were found in the same batch of crystal whereas 32*H* was found in a different batch.