Multiple inter-slice diffuse scattering

The deviation from kinematical diffuse scattering within a slice implies that multiple coherent diffuse scattering terms are appreciable within the range of atomic correlations. Under these circumstances it seems possible that the multiple incoherent diffuse scattering terms representing repeated scattering between uncorrelated regions of the crystal may also be appreciable. Such terms have been considered briefly in part I.

The calculation of such multiple inter-slice diffuse scattering would appear to be very complicated and prohibitively lengthy unless some severe approximations are made.

One possible basis for approximation is the assumption that the dynamical factors, $D_{mp}(\mathbf{u})$, are independent of crystal thickness. It has been shown by Fisher (1965, and private communication), for the case of kinematical scattering within a slice, that for a given $\mathbf{u}$, the dynamical factor $D(\mathbf{u})$ usually changes rapidly at first with increasing thickness and then oscillates about some limiting value. For copper–gold alloys the oscillations have a periodicity of about 100 Å or less. Hence if we deal with relatively thick crystals it is a good assumption in this case to take $D(\mathbf{u})$ as a constant when considering higher-order terms.

On this basis we may write the intensity for single diffuse scattering, given by (20), as

$$I_d^{(1)}(\mathbf{u}) = NI_d^0(\mathbf{u}) = \sum_{n=1}^{N} I_d^0(\mathbf{u}) \, ,$$

i.e. we assume that each slice, from 1 to N, gives the same contribution, $I_d^0(\mathbf{u})$, to the final diffuse scattering. Then the second order term, corresponding to double diffuse scattering is

$$I_d^{(2)}(\mathbf{u}) = \int \sum_{n=1}^{N} I_d^0(\mathbf{u}_1) \sum_{r=n}^{N} I_d^0(\mathbf{u}-\mathbf{u}_1)d\mathbf{u}_1$$
$$\simeq \tfrac{1}{2}N^2 I_d^0(\mathbf{u}) * I_d^0(\mathbf{u}) \, ,$$

and the total diffuse scattering will be

$$I_d(\mathbf{u}) = \sum_m I_d^{(m)}(\mathbf{u})$$
$$\simeq \mathcal{F}[\exp\{\mathcal{F}^{-1} I_d^0(\mathbf{u})\} - 1] \, . \quad (21)$$

On this basis the total effects of multiple inter-slice diffuse scattering could be calculated without a great deal of additional computation.

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Correction for Second-Order Diffuse X-ray Scattering in the Determination of the Elastic Constants of Crystals

By B.W. Lucas

*Crystallography Laboratory, Department of Physics, The City University, London, E.C.*1, *England*

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A new and improved method of allowing for second-order thermal diffuse X-ray scattering, close to a reciprocal-lattice point, is proposed; an appropriate equation for first- and second-order contributions is matched, by the method of least-squares, to the experimentally measured scattering data. A program was written for the I.C.T. 1905 computer and some $K[ABC]_{hkl}$ values for KCl were compared with those previously reported.

Introduction

Several investigators have shown that measurement of the thermal diffuse scattering of X-rays close to a reciprocal-lattice point provides values for elastic constants, which are – at least for cubic crystals – comparable to those found by other methods (Wooster, 1962). The diffuse intensity, due to the thermal motion of atoms within the crystals, may be considered as a sum of contributions from multiple photon–phonon interactions; increasing in complexity as the so-called 'order of scattering' increases (Laval, 1939). Only single (first-order scattering) and double (second-order scattering) interaction of the lattice phonons with the X-ray photon will be considered.

In previous studies, correction for second-order scattering was made by a process of approximations (Ramachandran & Wooster, 1951); provisional values for the elastic constants were first obtained, by neglecting the effect of second-order scattering entirely, and then the values so obtained used to find an approximate correction. New constants were calculated and so on, until convergencc to the final values resulted.

For the method of correction described here, the appropriate equation is matched, by the method of least-squares, to the experimentally measured scattering data.

Relationships and approximations used in the refinement process

The observed intensity of the diffuse scattering, close to a reciprocal lattice point, may be expressed in the following way:

$$I_d(\text{obs}) = I_{d1} + I_{d2} + I_{d3} + \ldots + I_b$$

(Laval, 1939), where

I_d(obs)	is the total diffuse intensity observed.
I_{d_1}	is the intensity of the thermal diffuse scattering due to the single interaction between an X-ray photon and a lattice photon (first-order scattering).
I_{d_2}	is the intensity of the thermal diffuse scattering due to two photon–phonon interactions (second-order scattering).
I_{d_3}	*etc.*
I_b	is the background scattering, which includes Compton, air and instrumental scattering.

If the background scattering, I_b, is deducted and higher than the second-order effects are neglected, the thermal diffuse intensity observed for each observation, I'_d(obs), may be approximated to:

$$I'_d(\text{obs}) = G\left(K[ABC]_{hkl} \cdot \frac{1}{R^2} + HK'[ABC]_{hkl} \cdot \frac{1}{R}\right),$$

where

$$G = I_0 \left[\frac{e^2}{mc^2}\right]^2 \frac{kT\Omega|F_T|^2 q^2 P}{2\mu\tau^2}$$

and

$$H = \tfrac{1}{2}\pi^3 kTq^2$$

(Ramachandran & Wooster, 1951).

I'_d(obs)	is the total diffuse intensity observed, less background, I_b.
I_0	is the intensity per unit area of cross-section of the direct beam
e	is the electronic charge
m	is the mass of the electron
c	is the velocity of light
k	is the Boltzmann constant
T	is the absolute temperature
τ	is the volume of the unit cell
$\lvert F_T\rvert$	is the structure amplitude at temperature T
q	is the distance, in reciprocal space, of the lattice point to the origin.
R	is the distance in reciprocal space from the point of observation to the nearest lattice point.
Ω	is the solid angle subtended by the detector aperture at the crystal.
P	is the polarization factor.
μ	is the linear absorption coefficient of the crystal.

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

and

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

ϱ is the crystal density

ξ_α, ($\alpha = 1,2,3$), are the amplitudes of the three acoustical waves having the wave vector R

V_α, ($\alpha = 1,2,3$), are their corresponding velocities.

$K[ABC]_{hkl}$ and $K'[ABC]_{hkl}$ are functions of only the elastic constants, the directional indices A, B, C and h, k, l (Ramachandran & Wooster, 1951).

If $K'[ABC]_{hkl}$ is now approximated to $(K[ABC]_{hkl})^2$ (Prasad & Wooster, 1956*a,b*), the requirement for the least-squares method is that:

$$\sum_i [GH(K[ABC]_{hkl})^2 \cdot \frac{1}{R_i} + GK[ABC]_{hkl} \cdot \frac{1}{R_i^2} - I'_{d_i}(\text{obs})]^2,$$

should be a minimum. The summation is to be taken over all observations for each $K[ABC]_{hkl}$.

Results

The method was applied to the results obtained by Ramachandran & Wooster (1951) for KCl. An example of the rate of convergence of the method is given in Table 1.

Table 1. *Example of convergence rate*

Reciprocal lattice point: (440).
$G = 8{\cdot}7182 \times 10^{25}$ $(GH) = 4{\cdot}4920 \times 10^{29}$.

[*ABC*]	Refinement cycle	$K[ABC]_{440} \times 10^{12}$
[110]	(Initial value)	10·000 dyne^{-1} cm^2
	1	3·862
	2	3·195
	3	3·175
	4	3·176
	5	3·176

Table 2. *Comparison of some* $K[ABC]_{hkl}$ *values for* KCl

In each example, the initial value for $K[ABC]_{hkl}$ was put equal to $10{\cdot}000\times10^{-12}$ dyne^{-1}cm^2.

(hkl)	$[ABC]$	$K[ABC]_{hkl}$	G	GH	$K[ABC]_{hkl}\times10^{12}$ Value obtained	$K[ABC]_{hkl}\times10^{12}$ (Ramachandran & Wooster, 1951)
					(dyne^{-1}cm^2)	(dyne^{-1}cm^2)
(440)	[110]	$2/(C_{11}+C_{12}+2C_{44})$	$8{\cdot}7182\times10^{25}$	$4{\cdot}4920\times10^{29}$	3·176	3·09
	[010]	$\frac{1}{2}(1/C_{11}+1/C_{44})$			7·440	7·498
	[111]	$2/(C_{11}+2C_{12}+4C_{44})$ $+1/(C_{11}-C_{12}+C_{44})$			4·599	4·540
(400)	[100]	$1/C_{11}$	$12{\cdot}805\times10^{25}$	$3{\cdot}3028\times10^{29}$	2·277	2·28
	[110]	$1/(C_{11}-C_{12})$ $+1/(C_{11}+C_{12}+2C_{44})$			4·227	4·323

The refined values for $K[ABC]_{hkl}$ are shown in Table 2 and are compared with those obtained by Ramachandran & Wooster (1951) (last two columns).

Interpretation of the results

Analysis of the refined $K[ABC]_{hkl}$ values for (440) results in the following values for χ_1, and χ_2.

$$\chi_1(=C_{12}/C_{11})=0{\cdot}13 \quad \text{and} \quad \chi_2(=C_{44}/C_{11})=0{\cdot}19\,,$$

and therefore

$$C_{11}=4{\cdot}22\times10^{11}\ \text{dyne.cm}^{-2}$$
$$C_{12}=0{\cdot}55\times10^{11}\ \text{dyne.cm}^{-2}$$
$$C_{44}=0{\cdot}80\times10^{11}\ \text{dyne.cm}^{-2}\,.$$

From the corresponding values for (400) and $K[010]_{440}$ (this was chosen to complete the set of three simultaneous equations since it only involved two elastic coefficients),

$$\chi_1=0{\cdot}17 \quad \text{and} \quad \chi_2=0{\cdot}18\,,$$

and

$$C_{11}=4{\cdot}39\times10^{11}\ \text{dyne.cm}^{-2}$$
$$C_{12}=0{\cdot}74\times10^{11}\ \text{dyne.cm}^{-2}$$
$$C_{44}=0{\cdot}79\times10^{11}\ \text{dyne.cm}^{-2}\,.$$

(Variations of the two sets of values for the elastic constants, as a percentage of the *mean* values are:

$$C_{11}\sim6\%\,;\ C_{12}\sim29\%\,;\ C_{44}\sim1\%\,.)$$

Discussion

The method of analysis described for the treatment of the thermal diffuse intensity data results in values for $K[ABC]_{hkl}$ which are essentially similar to those obtained by Ramachandran & Wooster (1951); but is considerably more convenient in application and very much faster in actual use (*e.g.* an 8-cycle refinement takes only ~20 sec in computer time, for six observational points).

Variation in the measurement of C_{12} is shown by comparison of the results obtained from the two sets of data, (440) and (400). This has been pointed out also for values obtained, by X-ray measurement, with other substances; namely, iron pyrites (Prasad & Wooster, 1956*b*), lead (Prasad & Wooster, 1956*a*) and adamantane (Lucas, 1965). Uncertainty in the value of C_{12} appears to depend partially on the fact that C_{12} never occurs alone, as does C_{11} and C_{44}, in expressions for $K[ABC]_{hkl}$; but always in combination with C_{11} and usually C_{44} also. The effect of C_{12}-variation on $K[ABC]_{hkl}$ values is therefore small. This does set a limit to the accuracy with which C_{12} can be determined, irrespective of the apparent 'good agreement' between corresponding sets of observed intensity data (see Ramachandran & Wooster (1951) KCl results). It is therefore considered important for care to be taken in any averaging of elastic constant values (C_{12} in particular), which are derived from independent sets of data, and this should not disguise the inherent uncertainty of elastic constant values, obtained by the X-ray method, in any comparison made with those found by other methods.

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