The results of the whole calculation are the direction cosines of two rays which are treated symmetrically, *i.e.* reflected and reversed incident rays both leaving the crystal.

(b) Alternative settings of the axes

If data have been recorded using only one principal axis, it is immaterial whether this is *a*, *b* or *c*, as the axes and reflexion indices can readily be renamed. If however data have been recorded using two different axes (say *b* and *c*) for the same crystal, it is inconvenient (and productive of error) to have to define the crystal on two different sets of orthogonal axes. It is preferable to calculate the ray direction cosines for reflexions recorded with *b* as principal axis ($Z' \equiv b$) on the orthogonal axes $X'Y'Z'$, using Wells's formulae and then to convert these cosines to those for the same rays on the axes XYZ ($Z \equiv c$) used for definition of the crystal.

This may readily be done if the direction cosines of X, Y, and Z are known on the axes $X'Y'Z'$, as then

$$\cos \angle IX = \cos \angle IX' \cos \angle XX' + \cos \angle IY' \cos \angle XY'$$
$$+ \cos \angle IZ' \cos \angle XZ', \text{ etc.}$$

These direction cosines may be determined in the following way. Define a set of unit vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ along a^*, b^*, c^*. Then unit vectors $\mathbf{X}, \mathbf{Y}, \mathbf{Z}$ along X, Y, Z may be found in terms of these:

$$\mathbf{X} = \mathbf{a}$$
$$\mathbf{Y} = k\mathbf{a} + \mathbf{b}$$
$$\mathbf{Z} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c}.$$

$\mathbf{a}$ and $\mathbf{Y}$ are orthogonal, so

$$k\mathbf{a} \cdot \mathbf{a} + l\mathbf{b} \cdot \mathbf{a} = 0,$$

and $\mathbf{Y}$ is a unit vector, so

$$(k\mathbf{a} + l\mathbf{b})^2 = 1,$$

i.e.

$$k^2\mathbf{a} \cdot \mathbf{a} + l^2\mathbf{b} \cdot \mathbf{b} + 2kl\mathbf{a} \cdot \mathbf{b} = 1,$$

giving

$$k = -\mathbf{a} \cdot \mathbf{b}/D, \ l = 1/D,$$

where

$$D = [1 - (\mathbf{a} \cdot \mathbf{b})^2]^{1/2},$$

for $\mathbf{Y}$ on the same side of $\mathbf{a}$ as $\mathbf{b}$.

Similarly, as $\mathbf{Z}$ is orthogonal to both $\mathbf{a}$ and $\mathbf{b}$ we get

$$m = [(\mathbf{b} \cdot \mathbf{c})(\mathbf{a} \cdot \mathbf{b}) - \mathbf{c} \cdot \mathbf{a}]/DE$$
$$n = -m/(\mathbf{a} \cdot \mathbf{b}) - D(\mathbf{c} \cdot \mathbf{a})/E(\mathbf{a} \cdot \mathbf{b})$$
$$p = D/E$$

where

$$E = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}.$$

If $\mathbf{a} \cdot \mathbf{b} = 0$, the expression for n is indeterminate and it is given by

$$n = -p(\mathbf{b} \cdot \mathbf{c}).$$

In a similar way the components of the unit vectors $\mathbf{X}', \mathbf{Y}', \mathbf{Z}'$ may be found, for whichever permutation is required. Then if

$$\mathbf{X} = a_1\mathbf{a} + a_2\mathbf{b} + a_3\mathbf{c}$$

and

$$\mathbf{X}'b = {}_1\mathbf{a} + b_2\mathbf{b} + b_3\mathbf{c},$$

the required cosine $\angle X'X$ is given by

$$\mathbf{X} \cdot \mathbf{X}' = a_1b_1\mathbf{a} \cdot \mathbf{a} + a_1b_2\mathbf{a} \cdot \mathbf{b} + a_1b_3\mathbf{a} \cdot \mathbf{c} + \dots,$$

and similarly for the remaining angles.

These methods have been incorporated in a general absorption correction program written in Fortran for the Atlas Computer, using the method of De Meulenaer & Tompa (1965).

I would like to thank Dr R. E. Gaskell for the solution of the problem outlined in part (*b*).

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On the Bragg Reflexion from Ideal Absorbing Crystals

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The general analytic expression is given for the integral reflexion coefficient of X-rays from thick ideal absorbing crystals.

Introduction

In order to calculate the integral reflexion of X-rays from thick ideal crystals in the presence of an absorption, one has to utilize, in accord with the Prins method, the numerical integration of the well-known formula for the reflexion coefficient, in which the absorption is taken into account by adding the imaginary terms to the atomic scattering amplitudes. However, a simple analytic expression of the integral reflexion can be

given, which is valid for arbitrary ratios between real and imaginary parts of the atomic scattering amplitudes. In fact, the problem was solved in our recent paper (Kagan, Afanas'ev & Perstnev, 1968), where the interaction of the resonant γ-quanta with crystals containing Mössbauer nuclei has been studied. In that case, the role of absorption is of special importance owing to its relatively large value.

Bearing in mind the interest of this problem for the X-ray physicist, we shall give here a detailed derivation of the general formula for the integral intensity directly applicable to the case of X-rays.

Derivation of general formulae

The dynamical theory of X-ray diffraction gives the analytic form of the reflexion coefficient $R(\theta)$ in the Bragg case both for non-absorbing and for absorbing crystals (see, e.g. Zachariasen, 1946; Laue, 1961).

In the case of a thick crystal ($\mu t \gg l$) $R(\theta)$ takes the form

$$R(\theta) = \frac{C^2 \gamma_0 |\gamma_h| \, |\chi_h|^2}{|\gamma_0\alpha - \tfrac{1}{2}\chi_0(\gamma_0 + |\gamma_h|) \pm \sqrt{[\gamma_0\alpha - \tfrac{1}{2}\chi_0(\gamma_0 + |\gamma_h|)]^2 - C^2\gamma_0|\gamma_h|\chi_h\chi_{\bar{h}}|^2}} . \tag{1}$$

Here, α determines a deviation from the Bragg condition and is related to the angle θ (at $\alpha \ll 1$) through the expression

$$\alpha \simeq \sin 2\theta_B(\theta_B - \theta) ;$$

χ_h is the Fourier component of the polarizability per unit volume multiplied by 4π,

$$\chi_h = -\frac{e^2}{mc^2} \frac{\gamma^2}{\pi V_0} F_h ,$$

where F_h is a structure factor.

The remaining symbols are standard and correspond to those of Laue (1961).

The integral intensity,

$$R_i = \int_{-\infty}^{\infty} R(\theta)d\theta = \frac{1}{\sin 2\theta_B} \int_{-\infty}^{\infty} R(\alpha)d\alpha ,$$

can be easily transformed as follows

$$R_i = \frac{1}{\sin 2\theta_B} \left| \frac{\chi_h}{\chi_{\bar{h}}} \right| \int_{-\infty}^{\infty} (M - \sqrt{M^2 - 1})d\alpha , \tag{2}$$

where

$$M = \frac{|\gamma_0\alpha - \tfrac{1}{2}\chi_0(\gamma_0 + |\gamma_h|)|^2 + |[\gamma_0\alpha - \tfrac{1}{2}\chi_0(\gamma_0 + |\gamma_h|)]^2 - C^2\gamma_0|\gamma_h|\chi_h\chi_{\bar{h}}|}{C^2\gamma_0|\gamma_h| \, |\chi_h\chi_{\bar{h}}|} .$$

Going in the integral (2) from the variable α to the variable M we have

$$R_i = \frac{|C\chi_h|}{\sin 2\theta_B} \sqrt{2\left|\frac{\gamma_h\chi_h}{\gamma_0\chi_{\bar{h}}}\right|} \int_{M_0}^{\infty} \frac{(M - \sqrt{M^2 - 1}) \sqrt{M - M_0}}{M - M_0 + 2s^2} \cdot dM , \tag{3}$$

where

$$M_0 = 1 + 2s^2(1 - q^2) .$$

Here we introduced the notations

$$s = \frac{\gamma_0 + |\gamma_h|}{2\sqrt{\gamma_0|\gamma_h|}} \frac{Im\chi_0}{|C|\sqrt{|\chi_h\chi_{\bar{h}}|}} ,$$

$$q = \frac{2\sqrt{\gamma_0|\gamma_h|}}{\gamma_0 + |\gamma_h|} \frac{|C Im\sqrt{\chi_h\chi_{\bar{h}}}|}{Im\chi_0} . \tag{4}$$

The quantity s characterizes the relative role of an absorption and vanishes in non-absorbing crystals. The quantity q is mainly determined by the geometrical factors.

(For crystals with inversion centre we have $\chi_{\bar{h}} = \chi_h$ and thus

$$s = \frac{\gamma_0 + |\gamma_h|}{2\sqrt{\gamma_0|\gamma_h|}} \frac{Im\chi_0}{|C\chi_h|} , \quad q = \frac{2\sqrt{\gamma_0|\gamma_h|}}{\gamma_0 + |\gamma_h|} \frac{|C Im\chi_h|}{Im\chi_0} .$$

For the symmetric reflexion ($|\gamma_h| = \gamma_0$) we have

$$s = \frac{Im\chi_0}{|C\chi_h|} , \quad q = \frac{|C|Im\chi_h}{Im\chi_0} .)$$

Using the substitution

$$M - M_0 = 2s^2(1 - q^2) \frac{z^2}{1 - z^2}$$

and setting

$$k = [1 + s^2(1 - q^2)]^{-1/2} \tag{5}$$

the integral (3) can be transformed as follows

$$R_i = \frac{8}{3 \sin 2\theta_B} |C\chi_h| \sqrt{\left|\frac{\gamma_h\chi_h}{\gamma_0\chi_{\bar{h}}}\right|} P(s, q) , \tag{6}$$

where

$$P(s, q) = \frac{3\sqrt{1 - k^2}}{2(1 - q^2)k^3} (I_1 + I_2) ,$$

$$I_1 = \int_0^1 [2 - k^2 - k^2 z^2 - 2\sqrt{(1 - k^2)(1 - k^2 z^2)}]$$

$$\times \frac{q^2 dz}{(1 - q^2 z^2)\sqrt{1 - z^2}} ,$$

$$I_2 = \int_0^1 [2 - k^2 - k^2z^2 - 2\sqrt{(1-k^2)(1-k^2z^2)}]$$

$$\times \left[\frac{1-q^2}{(1-z^2)^{5/2}} - \frac{1}{(1-z^2)^{3/2}}\right] dz. \quad (7)$$

The integral I_1 is directly expressed through the full elliptic integrals $\mathbf{K}$ and Π of the first and the third type, respectively (Erdelyi, 1953).

$$I_1 = \frac{\pi}{2}k^2 + \frac{\pi}{2\sqrt{1-q^2}} \cdot [2q^2 - k^2(1+q^2)]$$

$$+ 2\sqrt{1-k^2}[(k^2-q^2)\Pi(-q^2,k) - k^2\mathbf{K}(k)]. \quad (8)$$

Integrating I_2 by parts we have

$$I_2 = \int_0^1 [2 - k^2 - k^2z^2 - 2\sqrt{(1-k^2)(1-k^2z^2)}]$$

$$\times d\left\{\frac{z}{3}\left[\frac{1-q^2}{(1-z^2)^{3/2}} - \frac{1+2q^2}{\sqrt{1-z^2}}\right]\right\}$$

$$= \tfrac{2}{3}k^2[(1-q^2)I_3 + I_4], \quad (9)$$

where

$$I_3 = \int_0^1 \left(1 - \sqrt{\frac{1-k^2}{1-k^2z^2}}\right) d\left(\frac{z}{\sqrt{1-z^2}}\right)$$

$$= \int_0^1 \frac{k^2\sqrt{1-k^2z^2}\,dz}{(1-k^2z^2)^{3/2}\sqrt{1-z^2}} = \frac{E(k)}{\sqrt{1-k^2}}$$

$$- \sqrt{1-k^2}\mathbf{K}(k) \quad (10)$$

and

$$I_4 = \int_0^1 \left(\sqrt{\frac{1-k^2}{1-k^2z^2}} - 1\right)\frac{1-q^2+(1+2q^2)z^2}{\sqrt{1-z^2}} \, dz$$

is expressed again in the elliptic integrals

$$I_4 = (1-q^2)\left[\sqrt{1-k^2}\,\mathbf{K}(k) - \frac{\pi}{2}\right] + (1+2q^2)$$

$$\times \left\{\frac{\sqrt{1-k^2}}{k^2}[\mathbf{K}(k)-E(k)] - \frac{\pi}{4}\right\}. \quad (11)$$

Here, E is the full elliptic integral of the second type. Now, using the formulas (7)–(11) we get finally

$$P(s,q) = (1-s^2-2q^2s^2)\frac{E(k)}{k} - \frac{3\pi}{4}s(1-2q^2s^2)$$

$$+ ks^2(1-q^2)[3(1-q^2s^2)\Pi(-q^2,k)$$

$$- (2-s^2-2q^2s^2)\mathbf{K}(k)]. \quad (12)$$

Thus with the use of the introduced notations (4) and (5), the expressions (6) and (12) completely solve the problem of the integral reflexion from a thick absorbing single crystal, without any restriction on the absorption power.

Table 1. The function $P(s,q)$ for various s and q

q \ s	5·00	3·00	2·00	1·50	1·00	0·90	0·80	0·70	0·60	0·50	0·45	0·40	0·35	0·30	0·25	0·20
1·0	0·059	0·097	0·143	0·190	0·280	0·304	0·349	0·412	0·473	0·516	0·541	0·568	0·599	0·633	0·672	0·716
0·9				0·187	0·271	0·295	0·332	0·383	0·451	0·496	0·523	0·552	0·584	0·620	0·661	0·708
0·7					0·266	0·290	0·323	0·366	0·423	0·471	0·499	0·529	0·564	0·602	0·646	0·696
0·5							0·318	0·356	0·406	0·455	0·484	0·515	0·551	0·591	0·636	0·687
0·3								0·352	0·397	0·446	0·475	0·507	0·543	0·583	0·630	0·682
0·1									0·392	0·442	0·470	0·503	0·539	0·580	0·627	0·680

Weak absorption case

Using expressions (6) and (12) and tables of the elliptic integrals one can easily calculate the integral intensity in every concrete situation. However, in most cases of practical interest the expression (12) can be simplified. As a rule, with the exception of some of the cases near an absorption edge, the X-ray absorption is small, so that $Im\chi_0 \ll |\chi_0|$ and, if the structure factor F_h is not accidently close to zero and if the polarization factor C is not too small, the quantity s is small compared with unity.

In such a case the parameter k is close to unity (note that $q \le 1$ always). Now using the expressions of the full elliptic integrals of the first and second type (Gradstein & Ryzhik, 1963) and the expansion

$$(1-q^2)\Pi(-q^2,k) \simeq \tfrac{1}{2} \ln \left(\frac{8}{1+q} \frac{1-q}{1-k} \right)$$

$$+ \frac{1-q}{4} \ln \frac{1+q}{1-q} , \ldots (1-k \ll 1) \qquad (13)$$

we find

$$P(s,q) \simeq 1 - \frac{3\pi}{4} s(1-2q^2s^2) + 3s^2 \left[\frac{1+q^2}{2} \ln \frac{4}{s(1+q)} \right.$$

$$\left. - \frac{1+3q^2}{4} + \frac{(1-q)^2}{4} \ln \frac{1+q}{1-q} \right]. \qquad (14)$$

The formula (14) has the simple analytic form and, for $s \le 0.2$ (which occurs for most real situations) it gives an accuracy of more than one per cent. For $s \lesssim 0.05$

the main terms in (14) are

$$P(s,q) \simeq 1 - \frac{3\pi}{4} s$$

and the integral reflexion takes the very simple form

$$R_i = \frac{8}{3 \sin 2\theta_B} \left(\sqrt{\left| \frac{\gamma_h \chi_h}{\gamma_0 \chi_{\bar{h}}} \right|} |C\chi_h| \right.$$

$$\left. - \frac{3\pi}{4} \frac{\gamma_0 + |\gamma_h|}{2\gamma_0} \left| \frac{\chi_h}{\chi_{\bar{h}}} \right| Im\chi_0 \right). \qquad (15)$$

This result is very close to the empirical result received by Hirsch & Ramachandran (1950), where instead of $3\pi/4$ they have 2·4. Setting $Im\chi_0 = 0$ we get the well-known Darwin result.

If $s > 0.2$ then one has to use the general expression (12) for $P(s,q)$. We have tabulated the function $P(s,q)$ and the results are given in Table 1.

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Representational Surfaces for Thermal Motion

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Representational surfaces for the mean-square displacement, and the root-mean-square displacement, are derived for atomic thermal motion in the harmonic approximation. It is shown how the form of these surfaces depends on the way in which 'mean-square displacement' is defined. It is concluded that to represent atomic thermal motion a different surface may be required from the second-order (ellipsoidal) surface usually presented in reports of crystal structure determinations.

Introduction

The purpose of this article is to clarify the meaning of the 'thermal vibration ellipsoids' presented graphically, stereographically, or parametrically in reports of crystal structure determinations to represent atomic thermal motion in the harmonic approximation.

Provided the forces acting on any atom are linear in the relative displacements of the atoms (the har-

monic approximation), it may be shown (Lipson & Cochran, 1966, p. 300) that the probability of the atomic centre lying within a volume element $dx_1 dx_2 dx_3$ is $p(x_1 x_2 x_3) dx_1 dx_2 dx_3$, where

$$p(x_1 x_2 x_3) =$$

$$[(2\pi)^{3/2} u_1 u_2 u_3]^{-1} \exp [-(x_1^2/2u_1^2 + x_2^2/2u_2^2 + x_3^2/2u_3^2)]. \qquad (1)$$

x_1, x_2, and x_3 are displacements along orthogonal axes