$\Delta\theta$ can easily vary by three orders of magnitude from 10^{-4} degrees to 10^{-1} degrees as electron density, wavelength and angles vary. For example, δ differs by a factor of 70 when comparing silicon irradiated with Mo $K\alpha$ radiation ($\delta = 0{\cdot}158\times10^{-5}$) to tungsten irradiated with Cr $K\alpha$ ($\delta = 11{\cdot}0\times10^{-5}$). When $\varphi = 0$, $1/\sin 2\theta$ varies from 5·75 to 1 as 2θ changes from 10 to 90° and when φ is slightly less than θ (*i.e.* grazing incidence) the trigonometric term in the expression for $\Delta\theta$ can be large. For example when $\theta-\varphi = 1{\cdot}0°$, $1/\tan(\theta-\varphi) = 57{\cdot}3$.

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On Integrated Intensities in Kato's Statistical Diffraction Theory

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Abstract

A new approach to Kato's [*Acta Cryst.* (1980), A**36**, 763–769, 770–778] calculations in the Laue case is presented, giving a clearer and simpler derivation of the mixed terms of the integrated intensities (Bragg- and forward-diffracted beams). The results are in agreement with calculations by Al Haddad & Becker [*Acta Cryst.* (1988), A**44**, 262–270] showing the necessity of correcting two errors in the original treatment of Kato.

I. Introduction

The statistical theory of Kato (1980*a*, *b*) is an outstanding contribution to diffraction theory because it spans in principle the whole range of crystal perfection, from perfect to ideally imperfect (extinction-free) crystals. The 'lattice phase factor' $\exp[i\mathbf{g}\,.\,\mathbf{u}(x, y, z)]$ which characterizes the crystal distortion in the wave-optical Taupin–Takagi equations (Kato, 1976) [$\mathbf{g}$ is the diffraction vector and $\mathbf{u}(x, y, z)$ is the displacement field] is considered as a random function characterized by a static Debye–Waller factor E and a correlation length τ. In the present state of the theory the condition $\tau \ll \Lambda$, Λ being the extinction length, is assumed.

$E=0$ is the case of secondary extinction, for which diffraction from the incident direction (O beam) to the Bragg direction and conversely is entirely described by intensity-coupling equations (incoherent multiple scattering). $E=1$ is the case of perfect crystals, for which the O and G beams are coherent. For other values of E ($0<E<1$), the coherent waves are attenuated, even if the crystal is not absorbing, because anywhere in the crystal a diffraction event may transfer them into incoherent beams named the 'mixed' components of the O and G beams. There are also the purely incoherent components, the only ones present if $E=0$, which are built by diffraction of the incident undiffracted wave into the incoherent G beam directly and then distributed between the O and G beams.

In Kato (1980*b*), the coherent (I_0^c and I_g^c), the purely incoherent (I_0^i and I_g^i) and the mixed (I_0^m and I_g^m) intensity distributions are calculated as functions of the (s_0, s_g) coordinates of Fig. 1, for an incident beam limited by an infinitely narrow slit on the front face of a parallel-sided crystal in the Laue case. Integration of these distributions on the back face of the crystal of thickness t gives the following terms of the forward and Bragg integrated intensities expressed as

$$R_0(t) = R_0^c(t) + R_0^i(t) + R_0^m(t)$$
$$R_g(t) = R_g^c(t) + R_g^i(t) + R_g^m(t).$$

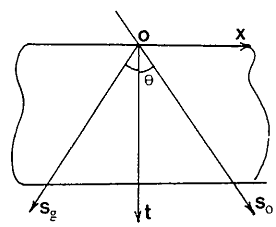

Fig. 1. Illustration of the (s_0, s_g) and (x, t) coordinates. $x = (s_0 - s_g)\sin\theta_B$; $t = (s_0 + s_g)\cos\theta_B$.

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Such calculations are very complicated in the case of the mixed terms. A new approach is presented here. It is shown in § II that $R_0^m(t)$ and $R_g^m(t)$ are solutions of simple transfer equations which are easy to solve and give solutions different from those found in Kato (1980*b*). The differences are then shown to be completely justified by errors in Kato's original treatment, these errors being pinpointed in § III (more physically) and in § IV (more mathematically). The new expressions are thus to be considered as the correct ones. They have also been obtained recently by Al Haddad & Becker (1988) (their paper was published just before the present one was submitted for publication). Their mathematical treatment is similar to that of Kato and is more complicated than the present one.

We use notations close to those of Kato, but simplified, because we assume a real structure factor and symmetrical Laue geometry. μ_0 is the absorption coefficient. τ_e (correlation length for the incoherent components) is supposed to be independent of τ. We write

$$H=\lambda/(2\Lambda\sin 2\theta_B) \qquad Z=E/(\Lambda\cos\theta_B)$$
$$\sigma=2\tau/\Lambda^2 \qquad \tilde{\sigma}=2\tau_e/\Lambda^2$$
$$L=\sigma/\cos\theta_B \qquad M=(1-E^2)L+\mu_0/\cos\theta_B$$
$$\tilde{L}=\tilde{\sigma}/\cos\theta_B \qquad \tilde{M}=\tilde{L}+\mu_0/\cos\theta_B$$
$$\mu_e=\mu_0+(1-E^2)\sigma \qquad \tilde{\mu}_e=\mu_0+\tilde{\sigma}.$$

We shall refer to Kato's papers (1980*a*, *b*), as Kato I and Kato II respectively; for instance, the formulas for the coherent integrated intensities are

$$\left.\begin{aligned}R_0^c(t)&=EH[2Zt-W(2Zt)]\exp(-Mt)\\ R_g^c(t)&=EH\,W(2Zt)\exp(-Mt)\end{aligned}\right\}\quad (1)\ \text{(Kato II, 26)}$$

where $W(x)$ is the Waller function, defined as

$$W(x)=\int_0^x \mathrm{d}u\,J_0(u).$$

II. Differential transfer equations for $R_0^m(t)$ and $R_g^m(t)$ and their solutions

The intensity-coupling equations (Kato I, 28) contain a source term proportional to the intensity of the incident undiffracted beam for the purely incoherent distributions and source terms proportional to the coherent distributions $I_0^c(s_0, s_g)$ and $I_g^c(s_0, s_g)$ for the mixed distributions $I_0^m(s_0, s_g)$ and $I_g^m(s_0, s_g)$. These are thus solutions of

$$\begin{aligned}\partial I_0^m/\partial s_0&=\tilde{\sigma}I_g^m(s_0, s_g)-\tilde{\mu}_e I_0^m(s_0, s_g)\\ &\quad+(1-E^2)\sigma I_g^c(s_0, s_g)\\ \partial I_g^m/\partial s_g&=\tilde{\sigma}I_0^m(s_0, s_g)-\tilde{\mu}_e I_g^m(s_0, s_g)\\ &\quad+(1-E^2)\sigma I_0^c(s_0, s_g).\end{aligned}\qquad (2)$$

The boundary conditions are

$$\begin{aligned}&I_0^m(s_0, s_g) \quad\text{and}\quad I_g^m(s_0, s_g)=0\\ &\text{for } s_0=0 \quad\text{and}\quad \text{for } s_g=0.\end{aligned}\qquad (3)$$

The derivatives in (2) can be expressed as (see Fig. 1)

$$\partial I/\partial s_0,\ \partial I/\partial s_g=\pm\sin\theta_B\,\partial I/\partial x+\cos\theta_B\,\partial I/\partial t.$$

The mixed and coherent components of the integrated intensities are introduced by integrating over x, from $(-t\tan\theta_B)$ to $(+t\tan\theta_B)$. Taking into account condition (3), we obtain simple transfer equations,

$$\begin{aligned}\mathrm{d}R_0^m/\mathrm{d}t&=\tilde{L}R_g^m(t)-\tilde{M}R_0^m(t)+(1-E^2)LR_g^c(t)\\ \mathrm{d}R_g^m/\mathrm{d}t&=\tilde{L}R_0^m(t)-\tilde{M}R_g^m(t)+(1-E^2)LR_0^c(t).\end{aligned}\qquad (4)$$

The functions

$$S(t),\ D(t)=R_0^m(t)\pm R_g^m(t)$$

are the solutions of

$$\begin{aligned}\mathrm{d}S/\mathrm{d}t+(\tilde{M}-\tilde{L})S(t)&=(1-E^2)L[R_g^c(t)+R_0^c(t)]\\ \mathrm{d}D/\mathrm{d}t+(\tilde{M}+\tilde{L})D(t)&=(1-E^2)L[R_g^c(t)-R_0^c(t)]\end{aligned}$$

which are equal to 0 for $t=0$. These solutions are

$$\begin{aligned}S(t),\ D(t)&=(1-E^2)L\int_0^t \mathrm{d}t'\exp[-(\tilde{M}\mp\tilde{L})(t-t')]\\ &\quad\times[R_g^c(t')\pm R_0^c(t')].\end{aligned}$$

$R_g^c(t)$ and $R_0^c(t)$ are given in (1). Using the quantities $m_{1,2}$ and n_2 defined in (Kato II, 32*a*, 33*a*),

$$\begin{aligned}m_{1,2}&=L\int_0^t \mathrm{d}t'\,2Zt'\exp(-Mt')\\ &\quad\times\exp[-(\tilde{M}\mp\tilde{L})(t-t')]\\ n_2&=L\int_0^t \mathrm{d}t'\,W(2Zt')\exp(-Mt')\\ &\quad\times\exp[-(\tilde{M}+\tilde{L})(t-t')],\end{aligned}$$

we can express the mixed terms as

$$\begin{aligned}R_0^m(t)&=E(1-E^2)H[\tfrac{1}{2}(m_1-m_2)+n_2]\\ R_0^m(t)&=E(1-E^2)H[\tfrac{1}{2}(m_1+m_2)-n_2].\end{aligned}\qquad (5)$$

III. Discussion of the modifications to Kato's formulas

These expressions (5) are to be compared with (Kato II, 36*a*, *b*). The differences are the factor $\frac{1}{4}$ and the quantities m_3 and n_3 present in Kato's formulas, but not in the new formulas (5).

First, it can be shown that the factors 2 in the formulas (Kato I, 30) defining σ and $\tilde{\sigma}$ have been later forgotten in writing (Kato II, 19). The factor $\frac{1}{4}$ must therefore be taken out.

It can also be checked that the other differences are cancelled if the correction

$$\cosh(\tilde{L}t)\quad\text{instead of}\quad[\cosh(Lt)-1]\qquad (6)$$

is made in (Kato II, 24a) defining the 'propagator' $K_0(t)$. The new $K_0(t)$ and the $K_g(t)$ of (Kato II, 24b) are solutions of the intensity transfer equations

$$\mathrm{d}K_0/\mathrm{d}t=\tilde{L}K_g(t)-\tilde{M}K_0(t)$$
$$\mathrm{d}K_g/\mathrm{d}t=\tilde{L}K_0(t)-\tilde{M}K_g(t)$$

with modified boundary conditions

$$\text{for } t=0\begin{cases}\tilde{L}K_0=1 \text{ instead of } 0\\ \tilde{L}K_g=0 \text{ unchanged.}\end{cases}$$

This means that the process of direct transmission (no diffraction event) after the coherent-to-mixed incoherent diffraction event is now taken into account. This simple process is illustrated by the diagrams of Fig. 2, which complement the diagrams of Kato (1980b, Fig. 1).

This discussion justifies the modification (6) to be introduced in Kato's calculations in order to obtain agreement with the new expressions (5) of the mixed terms.

Finally it can be shown that the error corrected by (6) originates in Kato's expressions of the mixed distributions (Kato II, 9b and 10a). For this reason, we consider in the next section his calculation (Kato, 1980b, § 2) based on the two-dimensional Laplace transformation

$$\overline{I}(p,q)=LT[I(s_0,s_g)]$$
$$=\int_0^\infty\int_0^\infty \mathrm{d}s_0\,\mathrm{d}s_g\exp(-ps_0-qs_g)I(s_0,s_g).$$

IV. Correcting the mixed intensity distributions

The Laplace transforms of the partial derivatives in (2) are

$$LT(\partial I_0^m/\partial s_0)=p\overline{I_0^m}(p,q)-\int_0^\infty \mathrm{d}s_g\exp(-qs_g)I_0^m(0,s_g)$$

$$LT(\partial I_g^m/\partial s_g)=q\overline{I_g^m}(p,q)-\int_0^\infty \mathrm{d}s_0\exp(-ps_0)I_g^m(s_0,0),$$

in which the integrals are here equal to 0, because of condition (3). Then (2) are transformed to

$$(p+\tilde{\mu}_e)\overline{I_0^m}-\tilde{\sigma}\overline{I_g^m}=(1-E^2)\sigma\overline{I_g^c}(p,q)$$
$$(q+\tilde{\mu}_e)\overline{I_g^m}-\tilde{\sigma}\overline{I_0^m}=(1-E^2)\sigma\overline{I_0^c}(p,q),$$

or

$$\overline{I_0^m}=(1-E^2)\sigma[\overline{A}(q+\tilde{\mu}_e,p+\tilde{\mu}_e)\overline{I_g^c}+\tilde{\sigma}\overline{G}(p+\tilde{\mu}_e,q+\tilde{\mu}_e)\overline{I_0^c}]$$
$$\overline{I_g^m}=(1-E^2)\sigma[\overline{A}(p+\tilde{\mu}_e,q+\tilde{\mu}_e)\overline{I_0^c}+\tilde{\sigma}\overline{G}(p+\tilde{\mu}_e,q+\tilde{\mu}_e)\overline{I_g^c}],$$

with

$$\overline{G}(p,q)=(pq-\tilde{\sigma}^2)^{-1}=(1/pq)\sum_0^\infty(\tilde{\sigma}^2/pq)^n$$

$$\overline{A}(p,q)=pG(p,q)=1/q+(1/q)\sum_1^\infty(\tilde{\sigma}^2/pq)^n.$$

These expansions are convenient for calculating the inverse transforms of $\overline{G}(p,q)$ and $\overline{A}(p,q)$:

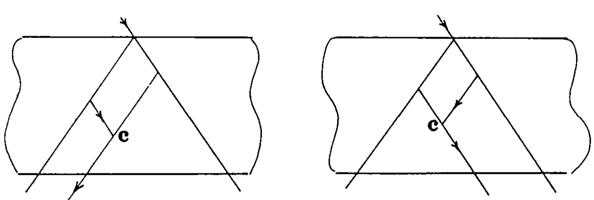
$$G(s_0,s_g)=\sum_0^\infty[\tilde{\sigma}(s_0s_g)^{1/2}]^{2n}/(n!n!)$$
$$=I_0[2\tilde{\sigma}(s_0s_g)^{1/2}]$$
$$A(s_0,s_g)=\tfrac{1}{2}\delta(s_0)+\tilde{\sigma}(s_0/s_g)^{1/2}$$
$$\times\sum_1^\infty[\tilde{\sigma}(s_0s_g)^{1/2}]^{2n-1}/[n!(n-1)!]$$
$$=\tfrac{1}{2}\delta(s_0)+\tilde{\sigma}(s_0/s_g)^{1/2}I_1[2\tilde{\sigma}(s_0s_g)^{1/2}],$$

where I_0 and I_1 are modified Bessel functions. The δ function in the last expression has been omitted in Kato's calculations. This omission explains the error in the propagator $K_0(t)$ discussed in the preceding section.

The correct formulas for the mixed intensity distributions are obtained by the substitutions

$$(s_0/s_g)^{1/2}I_1[2\tilde{\sigma}(s_0s_g)^{1/2}]$$
$$\to\delta(s_0)/2\tilde{\sigma}+(s_0/s_g)^{1/2}I_1[2\tilde{\sigma}(s_0s_g)^{1/2}]$$
in (Kato II, 9b)

$$(s_g/s_0)^{1/2}I_1[2\tilde{\sigma}(s_0s_g)^{1/2}]$$
$$\to\delta(s_g)/2\tilde{\sigma}+(s_g/s_0)^{1/2}I_1[2\tilde{\sigma}(s_0s_g)^{1/2}]$$
in (Kato II, 10a).



(a) (b)

Fig. 2. The coherent waves which are transformed to incoherent beams at point C may then be transmitted directly, giving a contribution to (a) the mixed G beam or (b) the mixed O beam.

V. Concluding remarks

The corrected forms of the mixed integrated intensities differ significantly from Kato's original expressions. We need not go into details here, since this is discussed in the paper by Al Haddad & Becker (1988), in which plots of integrated intensities as functions of $(t/\Lambda \cos\theta_B)$ are given and can be compared with those in Kato II (Figs. 2 and 3).

In the Kato and in the Al Haddad & Becker treatments, the mixed integrated intensities are obtained *via* the intensity distributions $I_0^m(s_0, s_g)$ and $I_g^m(s_0, s_g)$. This is not the case in our approach based on the simple transfer equations and which only requires very simple mathematics.

The statistical diffraction theory will probably be developed much further. There are many open questions, for instance the relation between the correlation lengths τ and τ_e. Efforts will be made to overcome the limitation $\tau \ll \Lambda$. Such questions have not been considered in the present paper which is strictly devoted to Kato's equations in the form defined in Kato (1980*a*).

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A Time-of-Flight Neutron Diffraction Study of Anharmonic Thermal Vibrations in SrF_2, at the Spallation Neutron Source ISIS

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Abstract

Measurements have been made, at wavelengths in the range 0·3-6·2 Å, of *hhl* reflections of SrF_2 on the single-crystal diffractometer (SXD) at the ISIS Spallation Neutron Source. After application of a variable-wavelength extinction correction to the derived $|F_{hkl}|$ values, a refinement of the anharmonicity parameter β_F of the fluorine atoms was carried out, yielding a value of $-4{\cdot}19\,(30)\times10^{-19}$ J Å^{-3}.

Introduction

The anharmonic thermal vibrations of the tetrahedrally bound atoms in fluorite structures have been widely studied using monochromatic neutron beams from reactor sources (Cooper, Rouse & Willis, 1968; Cooper & Rouse, 1971; Mair & Barnea, 1971; Mair, Barnea, Cooper & Rouse, 1974). The purpose of this study was to investigate, as part of the commissioning of the single-crystal diffractometer (SXD) at ISIS, a well characterized sample of SrF_2 using the white-beam neutrons from a pulsed source and to demonstrate the advantages of a pulsed source for high-resolution studies exploiting the high flux of shorter-wavelength neutrons. The measurements were carried out using a single (20 × 20 mm) scintillator detector while SXD awaits the completion of a 300 × 300 mm Anger camera position-sensitive detector (Forsyth, Lawrence & Wilson, 1988).

The simplest potential describing the anharmonic thermal vibrations in the strontium fluoride structure is (Cooper, Rouse & Willis, 1968)

$$V_j(\mathbf{r}) = V_{0j} + \tfrac{1}{2}\alpha_j(x_j^2+y_j^2+z_j^2) + \beta_j(x_jy_jz_j) \qquad (1)$$

where j = Sr, F and x_j, y_j and z_j are the coordinates of the thermal displacement of the jth atom. The $(x_j^2+y_j^2+z_j^2)$ term is the normal harmonic potential with α_j related to the mean square displacement of atom j and the term in β_j reflects the contribution of anharmonicity to the third-order term in the potential.

Owing to the centrosymmetry at the Sr site, $\beta_{Sr} = 0$. However β_F for the tetrahedrally bonded fluorine atoms has an appreciable effect on the observed intensities for reflections where the sum of indices $|h|+|k|+|l| = 4n \pm 1$. After Mair & Barnea (1971) we can write for the ratio of two structure factors

$$|F_+|/|F_-| = 1-(2b_F/b_{Sr}) \times \exp\left[(B_{Sr}-B_F)\left(\frac{h^2+k^2+l^2}{4a^2}\right)\right] \times (B_F/4\pi a)^3(\beta_F/kT)(|h_1k_1l_1|+|h_2k_2l_2|) \qquad (2)$$

where $|F_\pm|$ are the structure factors for reflections *hkl* with $|h|+|k|+|l| = 4n \pm 1$, b_{Sr} and b_F are the scattering

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