# On the correction for thermal diffuse scattering in measured integrated intensities from cubic single crystals.

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An expression is obtained for the spherically averaged acoustic phonon polarization and velocity factor found in theories of 1-phonon thermal diffuse scattering that is valid for all real cubic crystals and easy to evaluate numerically. A comparison with the usual approximate form shows appreciable discrepancies for very anisotropic materials.

Nilsson (1957) derived an approximate relation for the contribution of first order thermal diffuse scattering to measured integrated intensities of Bragg reflections from cubic single crystals which involved a multiplicative factor $\mathcal{K}$, representing a spherical average of polarization and phase velocity terms for phonons of a given, small, wave vector magnitude. The expression obtained for $\mathcal{K}$ required the integral of a rather complicated function, so Nilsson suggested a much simpler form as an approximation, and this simpler form has been used in subsequent modifications and extensions of Nilsson's approach by Annaka (1962) and Cooper & Rouse (1968). Schwartz (1964) showed that Nilsson's general expression for $\mathcal{K}$ was limited by implicit assumptions concerning the elastic constants and gave the complete, unrestricted expression, and he tried to reduce this expression to a form that could be integrated numerically for those cases where the general expression showed apparent singularities within the range of integration. The purpose of the present note is to point out that the final reduced expression given by Schwartz is incorrect because of cancellation errors, to give a correct reduced expression, valid for all real cubic crystals, that is well behaved and easily evaluated numerically, and to compare values obtained from this expression with those from Nilsson's approximate form for a number of materials.

Schwartz's equation (4) gives the complete expression for $\mathcal{K}$, applicable to all cubic crystals, as

$$\mathcal{K} = \int_0^1 \left[ \frac{A}{(Cx^2 - D)} + \frac{2(-BD - AE + BCx^2 + ACx^4 - ACx^6)}{(Cx^2 - D)[I(x^2)]^{\frac{1}{2}}} \right] dx, \quad (1)$$



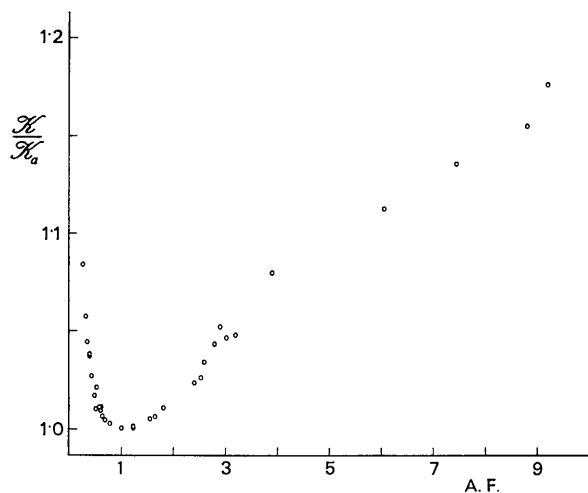Fig. 1. $\mathcal{K} / \mathcal{K}_a$ vs anisotropy factor for various materials.

where

$$A = (C_{11} - C_{12} - 2C_{44})(C_{11} + C_{12}) = b_1(C_{11} + C_{12}),$$
$$B = C_{44}(2C_{11} + C_{44}),$$
$$C = b_1^2(C_{11} + 2C_{12} + C_{44}),$$
$$D = -b_1(C_{11} + C_{12})C_{44},$$
$$E = C_{11}C_{44}^2,$$

and

$$I(x^2) = 4E^2 - ED + (D^2 - 6ED + EC)x^2$$
$$+ (D^2 - CD + 7ED - 2EC)x^4 + (EC - 5D^2 + 3CD)x^6$$
$$+ (3D^2 - 3CD)x^8 + CDx^{10}.$$

The singularity that apparently occurs if $Cx^2 - D = 0$ within the range of integration cannot be real, given that the integral represents a spherical average of a quantity that is everywhere positive and finite, so one can expect to be able to eliminate it. By straightforward separation and factoring of terms one can write:

$$I(x^2) = 4[E - D(x^2 - x^4)]^2 \cdot J(x^2), \quad (2)$$

where

$$J(x^2) = 1 + \frac{(Cx^2 - D)(1 - x^2)^2}{4[E - D(x^2 - x^4)]}. \quad (3)$$

Substituting this in equation (1), combining and rearranging terms, and clearing a radical in the numerator, we obtain finally:

$$\mathcal{K} = \int_0^1 \frac{B + A(x^2 - x^4) + \frac{1}{4}A(1 - x^2)^2 [(J(x^2))^{\frac{1}{2}} + 1]^{-1}}{[E - D(x^2 - x^4)](J(x^2))^{\frac{1}{2}}} dx. \quad (4)$$

The factors in the denominator can each become zero only if $C_{44}$ or $(C_{11} - C_{12})$ is negative or zero, which cannot happen for real crystals, so the integrand here is always well behaved and the integral is easily evaluated by numerical means.

This expression is equivalent to just the third term, the integral of the function, $G(x)$, in Schwartz's final equation. The first two terms in that equation did not cancel each other as they should because of an earlier error in considering cancellation effects.

In this same nomenclature, Nilsson's approximate form is:

$$\mathcal{K}_a = \frac{B + A/5}{E - D/5 + C/105}$$

Values of the ratio, $\mathcal{K} / \mathcal{K}_a$, have been calculated for 33 cubic materials using equations (4) and (5) and are plotted in Fig. 1 *vs* their appropriate anisotropy factors, A.F. = $2C_{44}/(C_{11} - C_{12})$. The elastic constant values were taken

from the *American Institute of Physics Handbook* (1963), with two exceptions: ordered $Cu_3Au$, from Flinn, McManus & Rayne (1960), and $\beta$-CuZn, from McManus (1963). The results for KCl and NaCl are in good agreement with the values given by Nilsson, but, contrary to Schwartz's results for $Cu_3Au$, no case was found for which $\mathscr{K}$ was less than $\mathscr{K}_a$. The discrepancy between $\mathscr{K}$ and $\mathscr{K}_a$ varies more or less systematically as a function of the anisotropy factor parameter, increasing with increasing departures from isotropy in either sense. The magnitude of the discrepancy is appreciable for very anisotropic materials.

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# Location of the anomalous scatterer in neutron anomalous scattering studies.

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A method is suggested for obtaining a Patterson map which contains only vectors related to the atom giving rise to anomalous scattering. This map gives directly the position of the anomalous atom, and can be used in the first stage of the method suggested by Singh & Ramaseshan (1968) for the solution of the phase problem in neutron diffraction.

Singh & Ramaseshan (1968) have pointed out that in a structure determination by neutron diffraction, using the anomalous scattering of neutrons by nuclei such as $Cd^{113}$ and $Sm^{149}$ to phase the reflexions, there will be difficulty in locating the anomalous atom by the Patterson method. This arises because vectors $A - A$ between anomalously scattering atoms $(A)$ are obscured by $N - N$ vectors between normal atoms $(N)$, even if the $A - N$ vector peaks are removed by suitably combining the intensity measurements on either side of the resonance wavelength $(\lambda_0)$. To overcome this difficulty Singh & Ramaseshan (1968) have suggested an analytical method which combines data at two wavelengths to give $F_A^2$, the contribution due to $A$ atoms alone. The position of the $A$ atom can then be determined by a Patterson synthesis with $F_A^2$ as coefficients.

In this note we show that a Patterson map can be obtained directly, from data collected at two wavelengths, which is completely free of both $A - N$ and $N - N$ interactions and contains only $A - A$ vectors. The Patterson map is based on the Fourier cosine synthesis proposed by Okaya & Pepinsky (1961). The location of the $A$ atoms using this map is then straightforward.

In the case of a non-centric crystal containing atoms which scatter neutrons anomalously, the Patterson function is complex. Following Okaya & Pepinsky (1961), it can be written as

$$P(\mathbf{U}) = P_c(\mathbf{U}) - iP_s(\mathbf{U}) \quad \text{where}$$
$$P_c(\mathbf{U}) = \Sigma' \, (|F(\mathbf{H})|^2 + |F(\overline{\mathbf{H}})|^2) \cos 2\pi \mathbf{H} \cdot \mathbf{U} \quad \text{and}$$
$$P_s(\mathbf{U}) = \Sigma' \, (|F(\mathbf{H})|^2 - |F(\overline{\mathbf{H}})|^2) \sin 2\pi \mathbf{H} \cdot \mathbf{U} \, .$$

$\mathbf{H}$ is $(h,k,l)$, $\mathbf{U}=(u,v,w)$, and $\Sigma'$ is the summation over half of the reciprocal sphere.

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Where there is only one type of anomalously scattering atom in the unit cell, it can be shown from equations (12) and (13) of Okaya & Pepinsky's paper that

$$|F(\mathbf{H})|^2 + |F(\overline{\mathbf{H}})|^2 = \underset{\substack{A-A \\ \text{Pairs}}}{\Sigma} (b_A'^2 + \Delta b_A''^2) \cos 2\pi \mathbf{H} \cdot \mathbf{U}_{AA}$$
$$+ \underset{\substack{A-N \\ \text{Pairs}}}{\Sigma} b_A' b_N' \cos 2\pi \mathbf{H} \cdot \mathbf{U}_{AN} + \underset{\substack{N-N \\ \text{Pairs}}}{\Sigma} b_N' b_{N'}' \cos 2\pi \mathbf{H} \cdot \mathbf{U}_{NN}$$

and

$$|F(\mathbf{H})|^2 - |F(\overline{\mathbf{H}})|^2 = \underset{\substack{A-N \\ \text{Pairs}}}{\Sigma} \Delta b_A'' b_N' \sin 2\pi \mathbf{H} \cdot \mathbf{U}_{AN}$$

where $\mathbf{U}_{AA}, \mathbf{U}_{AN}, \mathbf{U}_{NN}$ are vectors between $AA, AN, NN$ atoms and the scattering factor of the anomalous scatterer
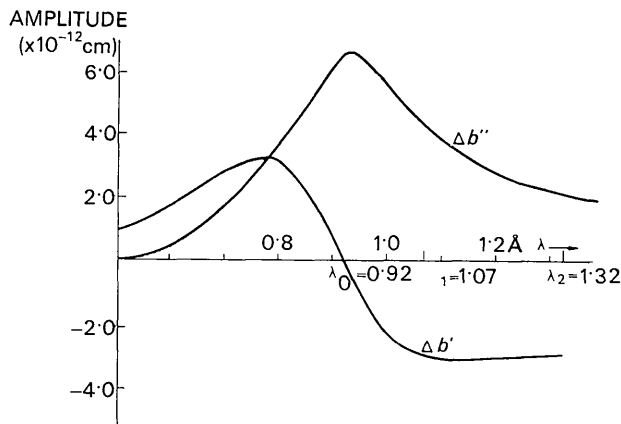
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Fig. 1. Wavelength dependence of $\Delta b'$ and $\Delta b''$ for $Sm^{149}$.