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Correction of the measured integrated intensities from cubic metallic single crystals for thermal diffuse scattering.*

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Nilsson (1957) has calculated the contribution to the measured integrated intensities from cubic single crystals due to the peaking of thermal diffuse scattering near Bragg reflections, and Chipman & Paskin (1959) have done this for powders. (These calculations only apply to ideally imperfect single crystals (Chipman & Batterman 1963).) It has been demonstrated by these authors that this term can be quite important when accurate integrated intensities are required for high-angle peaks. Nilsson expressed his results in the following form. If P is the measured and P_1 is the true integrated intensity of a peak at $2\theta_0$,

$$P = P_1(1+\alpha) \tag{1}$$

where $\alpha = a \sin 2\theta_0 K(\delta-\delta')/\lambda$. a is the near-neighbor distance, δ, δ' depend on the scanning ranges and $K = (4\pi k\varkappa/3a)\,(\sin^2\theta_0/2)T$. $\varkappa$ is a complicated function of the elastic constants. T is the temperature in degrees Kelvin. Because the treatment is in terms of the static elastic constants, dispersion is not taken into account. Implicit in Nilsson's treatment is an assumption about the relationship of the elastic constants which is violated by many metals. This occurs for

$$-(C_{11}-C_{12}-2C_{44})\,(C_{11}+C_{12})C_{44} > 0\,,$$

$$\frac{-(C_{11}+C_{12})C_{44}}{(C_{11}-C_{12}-2C_{44})(C_{11}+2C_{12}-C_{44})} < 1\,.$$

Here, Nilsson's results will be extended to include these cases.

$$\varkappa = \frac{Af_1(\theta,\varphi)+B}{Cf_2(\theta,\varphi)-Df_1(\theta,\varphi)+E} \tag{2}$$

where

$$\begin{aligned}
A &= (C_{11}-C_{12}-2C_{44})(C_{11}+C_{12}) = b_1(C_{11}+C_{12})\,,\\
B &= C_{44}(2C_{11}+C_{44})\,,\\
C &= b_1^2(C_{11}+2C_{12}+C_{44}) = b_1^2 b_2\,,\\
D &= -b_1(C_{11}+C_{12})C_{44}\,,\\
E &= C_{11}C_{44}^2\,,
\end{aligned}$$

$$f_1(\theta,\varphi) = \sin^4\theta \sin^2\varphi \cos^2\varphi + \sin^2\theta\cos^2\theta\,,$$

$$f_2(\theta,\varphi) = \sin^4\theta\cos^2\theta\sin^2\varphi\cos^2\varphi\,,$$

θ, φ are the polar coordinates of the spherical volume of integration.

Letting $x = \cos\theta$,

$$\varkappa = \frac{A(1-x^2)^2\sin^2\varphi\cos^2\varphi + [A(1-x^2)x^2+B]}{[C(1-x^2)^2x^2 - D(1-x^2)^2]\sin^2\varphi\cos^2\varphi - [D(1-x^2)x^2-E]}\,. \tag{3}$$

When integration with respect to φ is carried out the following expression is obtained:

$$\varkappa = \int_0^1 \frac{A\,dx}{Cx^2-D} + 2\int_0^1 \frac{(-BD-AE+BCx^2+ACx^4-ACx^6)dx}{(Cx^2-D)\sqrt{(I(x^2))}} \tag{4}$$

where

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

The first term in equation (4) may be written in closed form as

$$\int_0^1 \frac{A\,dx}{Cx^2-D} = \begin{cases} \dfrac{A}{\sqrt{(C|D|)}}\tan^{-1}\left(\sqrt{\dfrac{C}{|D|}}\right) & D<0 \\[2ex] \dfrac{A}{2\sqrt{(CD)}}\ln\dfrac{\sqrt{C}-\sqrt{D}}{\sqrt{C}+\sqrt{D}} & D>0\,. \end{cases}$$

The second term in equation (4) must be evaluated by numerical integration. This process is straightforward for $D<0$, but for $D>0$, $D/C<1$, there is a singularity at $x_0 = \sqrt{(D/C)}$. Writing the integrand of this term as $F(x)$, $F(x)$ is expanded about x_0 so that

$$\begin{aligned}
F(x) &= \frac{H(x_0)+H'(x_0)(Cx^2-D)+(1/2!)H''(x_0)(Cx^2-D)+\ldots}{(Cx^2-D)}\,,\\
&= \frac{H(x_0)}{(Cx^2-D)} + G(x)\,,
\end{aligned}$$

where $H(x) = F(x)(Cx^2-D)$ and the primes denote differentiation with respect to x. $G(x)$ has no singularities in the interval $0 \le x \le 1$ and may be evaluated by standard techniques. $H(x_0)/(Cx^2-D)$ is antisymmetric about x_0, positive and negative values cancelling at the positions $x_0 \pm x$ for $(2x_0-1) \le x \le 1$. $H(x_0)/(Cx^2-D)$ may be readily evaluated for the remaining interval $0 \le x \le (2x_0-1)$. When the separation was made, the following results were obtained:

$$H(x_0) = -A\,,$$

$$G(x) = \frac{\begin{aligned}\{&-(8ABE+4B^2D+A^2E)+(4B^2C-6A^2E+A^2D)x^2\\ &+(8ABC+7A^2E+A^2D)x^4-(8ABC-4A^2C+5A^2D)x^6\\ &+(3A^2D-8A^2C)x^8+4A^2Cx^{10}\}\end{aligned}}{\{2(-BD-AE+BCx^2+ACx^4-ACx^6)\sqrt{(I(x^2))}-AI(x^2)\}}$$

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Finally, then, for $D > 0$,

$$\varkappa = \frac{A}{2\sqrt{(CD)}} \ln \frac{\sqrt{C} - \sqrt{D}}{\sqrt{C} + \sqrt{D}} - A \int_0^{(2x_0-1)} \frac{dx}{(Cx^2 - D)} + \int_0^1 G(x)\, dx\,. \tag{5}$$

Nilsson (1957) has suggested a simple formula for $\varkappa$ derived by taking the mean values of each of the terms in the numerator and denominator of equation (2) separately:

$$\varkappa_{\text{appr.}} = \frac{\frac{1}{5}b_1(C_{11} + C_{12}) + C_{44}(2C_{11} + C_{44})}{\frac{1}{105}b_1^2 b_2 + \frac{1}{5}b_1(C_{11} + C_{12})C_{44} + C_{11}C_{44}^2}\,. \tag{6}$$

Table 1 shows a comparison between the values of $\varkappa_{\text{appr}}$ and $\varkappa$ obtained by numerical integration of equation (5) at intervals of 0·05 in x. The elastic constants used were those given by Flinn, McManus & Rayne (1960) for well ordered Cu_3Au. Of course, for other than monoatomic systems, alloys (such as Cu_3Au) or compounds of atoms of different masses, this correction does not take into account the more complex nature of the vibrational spectra. At the present time though, this is not possible and the type of correction discussed here is all that is presently feasible. The comparison of the two calculations in Table 1 shows the type of error that might occur, even with a monoatomic crystal.

It is clear that the exact formula, equation (5), should be used for the case $D > 0$, $D/C < 1$. By contrast, Nilsson (1957) showed that for KCl and NaCl, for which $D < 0$, the agreement was within a few percent.

Table 1. *$\varkappa$ for ordered* Cu_3Au

T	$\varkappa(10)^{12}$ $\text{cm}^2.\text{dyne}^{-1}$ (equation (5))	$\varkappa_{\text{appr}}(10)^{12}$ $\text{cm}^2.\text{dyne}^{-1}$ (equation (6))	Error (%)
77 °K	3·12	4·32	+38·4
298	3·91	4·62	+18·2

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Notes and News

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Reginald William James, 1891–1964

Sir Lawrence Bragg writes: R. W. James, who died in Cape Town on 7 July 1964, was one of the pioneers of X-ray crystallography. James graduated with first-class honours in Physics at Cambridge in 1912 and for two years carried out research in the Cavendish. In 1914 he was invited by Sir Ernest Shackleton to join his antarctic expedition as physicist, and when the *Endurance* was crushed by the ice and the party returned to England after its rescue, James joined the experimental Sound Ranging Section for locating enemy guns which had been established in Belgium under W. L. Bragg. Their close association in their war work naturally led to James joining Bragg at Manchester in 1919 when the latter was appointed Professor of Physics there. It was in this way that James entered the field of research in which he was to work for the rest of his life. He collaborated with Bragg and Bosanquet in the series of 'B.J.B.' papers from 1921 onwards which established the quantitative measurement of X-ray diffraction. Darwin had formulated the theory for perfect and imperfect crystals, and the intensive study of diffraction of sodium chloride as a standard 'mosaic' crystal, in particular the comparison of the integrated reflexion with the intensity of the incident beam, established the use of absolute values of $F(hkl)$ in X-ray crystallography. Two developments stemmed from this work. On the one hand James and his colleagues made a profound study of atomic scattering factors and the influence of thermal movements (Debye effect) and the quantitative measurements culminated in the well known paper by James, Hartree & Waller in which the zero-point energy was directly measured. On the other hand, absolute F values provided crystallographers with a means by which far more complex crystals could be tackled. James and Wood were responsible for one of the earliest of these investigations, the structure of barium sulphate, which has eleven parameters. This marked a great step forward at a time when it was widely doubted whether crystals with more than two parameters could be analysed with significant results. James's work at Manchester centred round the theory of X-ray diffraction and accurate quantitative measurement. His book *The Optical Principles of the Diffraction of X-Rays*, published in 1948, has a world-wide recognition as the standard text book on the subject.

In 1937 James was appointed Professor of Physics