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The refraction correction for lattice constants calculated from powder or rotation crystal patterns. By M. E. STRAUMANTIS, *University of Missouri School of Mines and Metallurgy, Department of Metallurgy, Rolla, Missouri, U.S.A.*

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It was recommended some years ago *not* to apply the refraction correction in the case of precision determination of lattice parameters from powder and rotation crystal photographs (Barrett, 1952). In the meantime some publications have appeared which have followed this recommendation, but in other cases the refraction correction has still been applied. The object of this communication is to point out when the refraction correction is necessary and when not.

Darwin (1914), and later Ewald (1918, 1920, 1924, 1925), developed a theory of X-ray diffraction from which it followed that the Bragg equation is correct only inside a crystal. This conclusion was later used by Stenström in order to determine the exact wavelength of X-rays in vacuum (or air). The equation used by him was (Siegbahn, 1931)

$$n\lambda' = 2d \sin \theta', \quad (1)$$

where λ' is the wavelength and θ' the reflection angle, both within the crystal.

λ' could be calculated from λ , the wavelength in air or vacuum, using the index of refraction μ :

$$\lambda' = \lambda/\mu; \quad (2)$$

the angle θ' follows from the observed Bragg angle θ , using Snell's law:

$$\cos \theta' = \cos \theta/\mu. \quad (3)$$

Eliminating λ' and $\cos \theta'$ from (1), and using (2) and (3), one obtains:

$$n\lambda = 2d(1 - \delta/\sin^2 \theta) \sin \theta, \quad (4)$$

where $\delta = 1 - \mu$. According to Siegbahn, (4) is identical with the equation derived by Ewald from his dynamical theory. The observed angle θ is larger than θ' , for which the Bragg equation is correct, and the d values calculated with θ will be slightly smaller than the actual ones. The refraction correction, to be added to the lattice

constant a of a cubic substance, is then, according to Ewald (see Lindh, 1930; Jette & Foote, 1935),

$$a = a_n(1 + \delta/\sin^2 \theta_n), \quad (5)$$

which can be derived directly from (4), and where a_n is the lattice constant as calculated from the n th interference. For more convenient application (calculation of δ from the dispersion theory), (5) is easily transformed:

$$a = a_n \left(1 + \frac{5 \cdot 4 a^2 \rho}{n^2 \Sigma h^2} \times 10^{-6} \right), \quad (6)$$

ρ being the density of the material under investigation, and $n^2 \Sigma h^2$ the sum of the squares of the indices (X-ray).

Equations (5) and (6) are strictly correct only in the case of reflection from a (large or small) surface of a single cubic crystal (Fig. 1, beam I). However, the path of the X-rays penetrating through single crystals is different, as reflection from the inside occurs without any deviation from Bragg's law (Fig. 1, beam II). This phenomenon was already known to the X-ray spectroscopists (cf. Meyer, 1934), and is explained by the fact that the beam II, bent away from normal N_{II} produces θ' , (equation (3)), which is now larger than θ by the amount

$$\theta' - \theta \doteq \Delta_r = (1 - \mu) \tan \theta,$$

and that this is exactly compensated by the effect of change in wavelength inside the crystal (equation (2)):

$$\theta' - \theta = \Delta_\lambda = -(1 - \mu) \tan \theta.$$

Thus the final result is that $\Delta_r + \Delta_\lambda = 0$, i.e. the X-ray beam II, passing under the angle θ' through the crystal, is reflected according to Bragg's law (Fig. 1).

No strong reflection will occur simultaneously from the surface of the crystal (beam I): because of refraction (normal N_I) and change in λ , the angle is now smaller than the internal Bragg angle θ' . Hence the crystal has to be turned from position II to I by the angle $\theta - \theta'$ to

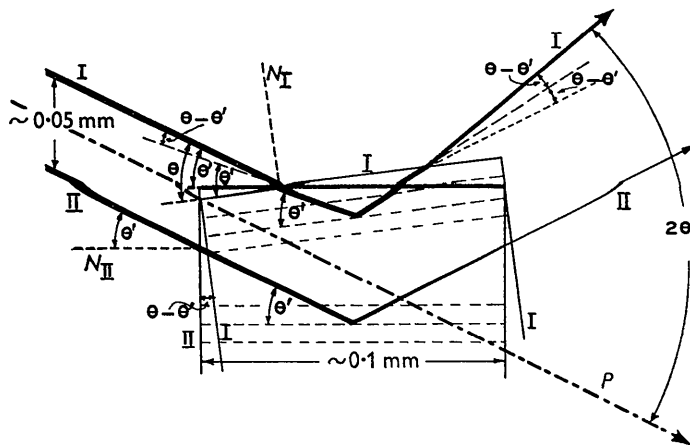


Fig. 1. Reflection of X-rays from the surface (beam I) and from the inside (beam II) of a cubic crystal. θ and θ' are the observed and actual angles of reflection.

Table 1. Lattice constants determined with Cu K and Cr K radiations, and the refraction correction, at $25.0 \pm 0.05^\circ \text{C}$.

Compound	All values in kX.					
	Not corrected			Corrected for refraction		
	a_{Cr}	a_{Cu}	$a_{\text{Cr}} - a_{\text{Cu}}$	a_{Cr}	a_{Cu}	$a_{\text{Cr}} - a_{\text{Cu}}$
LiF	4.01799	4.01805	-0.00006	4.01807	4.01808	-0.00001
NaF	4.62335	4.62341	-0.00006	4.62344	4.62345	-0.00001
As ₂ O ₃	11.05184	11.05194	-0.00010	11.05214	11.05208	+0.00006

produce a strong reflection beam from the surface.* As shown in Fig. 1, the total increase in angle is then $2(\theta - \theta')$, which has to be subtracted from the observed 2θ in order to get the actual angle of reflection θ' .

Because the intensity of beam II coming from the inside of the crystal is low owing to absorption, the intensest part of a powder line will be produced by those of the reflected X-ray beams which come from the surface of a rotating single crystal or from the surfaces of the crystal fragments (powder). This intensity will dominate the more, the stronger the absorption of the X-rays by the grains. Therefore, if in measuring the location of a powder or single-crystal line on a film the point of maximum density of the line on the equator of the pattern is determined, a refraction correction according to (5) or (6) has to be added to the calculated lattice parameter, as already pointed out previously (Straumanis, 1940, 1949, 1953).

Although brittle cubic crystals frequently disintegrate to small cubes during crushing (for instance the surface of pulverized potassium chloride is composed to the extent of 80% of (100) faces (Young, 1954)) there still will be plenty of grains of irregular shape in a powder sample. Besides, the X-ray beam impinges upon the grains at any angle (Fig. 1 shows the simplest position). This complicated situation was analysed by Wilson (1940) with the result that a correction has also to be added to the extrapolated (or calculated) lattice constant. According to Klug & Alexander (1954), the correction derived by Wilson is

$$a_{\text{corr.}} = a_{\text{obs.}}(1 + \delta) \quad (7)$$

It can be easily seen that (7) is also obtained from (5) if the angle approaches $\frac{1}{2}\pi$. Thus, (7) contains both kinds of correction, that due to the change in wavelength (equation (2)) and that due to refraction (equation (3)), but is strictly correct only for adding to lattice constants obtained by extrapolation to 90° , or calculated from high back-reflection angles. In the latter case, (7) naturally gives slightly smaller corrections than (5) or (6), but the difference can be disregarded. However, if constants are calculated from interferences under θ angles less than 80° , (5) or (6) should be used rather than (7). Anyway, the article of Wilson gives further evidence for the applicability of the equations (5) or (6) of Ewald for correction of lattice parameters calculated from powder and rotation crystal patterns.

As these refraction corrections are small, varying from approximately 0.00002 and less to 0.0002 Å (see also Frohnmeyer & Glocker, 1951, 1953), depending on the variables as given by (6), the application of the correction

gives sense only in the case of precision determinations. For such determinations both temperature control of the sample and reproducibility of measurements within a range smaller than or equal to the value as given by the calculated refraction correction, is required. In all other cases, or for purposes of comparison applying the same wavelength (Thewlis, 1955), the refraction correction can be omitted.

There is also some experimental evidence for the necessity of applying the refraction correction when calculating the constants from precision powder patterns.

All researchers who have used X-radiations of various wavelengths for measurements of lattice constants have felt that some correction is necessary to balance out the results obtained. As there were no other plausible reasons for deviations in the constants when using various wavelengths, equation (5) or (6) or a similar one was applied (Jette & Foote, 1935). The writer's previous measurements made with temperature-controlled samples also showed a decrease of the differences in lattice constants after the application of the correction (Straumanis, Ievinš & Karlsons, 1939, Table 1).

Finally, the X-ray-density atomic-weight determinations support the application of the same correction, for otherwise the weights would be too low when compared with those determined chemically (Straumanis, 1949, 1953). For instance, for the atomic weight of carbon as diamond, applying the above correction, 12.0096 was obtained (Straumanis & Aka, 1951). Disregarding the correction a value of only 12.0012 is obtained, which is too low as compared with the chemical weight 12.011. The refraction correction was also applied by the Hutchisons (1942, 1945) in determining the atomic weight of calcium and fluorine. Although they used data obtained with different X-radiations, and by various investigators, the calculated weights for each element, as computed from various combinations, agreed very well among themselves and with the chemical weights. The same was recently found in calculating the atomic weight of lithium (Hutchison, 1954). All these excellent results would not have been attained if the refraction correction were disregarded.

The precision lattice-parameter measurements of the writer and his associates, except the measurements of the years 1935, were all corrected for refraction using equation (6).

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* As $\theta - \theta'$ increases with decreasing θ , the reflections on Weissenberg photographs should appear more elongated at low angles than at high, a phenomenon which can frequently be observed.

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Oblique projections. By P. J. BLACK,* *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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The labour of investigating a three-dimensional structural pattern is usually reduced by the use of two-dimensional projections. Two such projections may be required to determine all the parameters of a structure, but in some systems (e.g. the cubic) a single projection will suffice. Calculations in three dimensions are sometimes necessary, even when the resulting increase in accuracy is not essential, in order to resolve atoms that overlap in the projections.

A unit cell is generally chosen to have a conventional relationship to the symmetry elements of a structure, and projections are usually made parallel to the sides of the cell. This is not a necessary restriction, and one can construct a projection parallel to any direction which joins two lattice points, i.e. parallel to any direction with rational zone indices. The term 'oblique projection' will be used to denote a projection parallel to a direction which is not the edge of a conventional unit cell.

In Fig. 1(a) is shown a projection, parallel to the two-fold axis, of two pairs of atoms in a structure of space group $P2$. A new cell may be chosen as in Fig. 1(b), and projection parallel to the axis b' gives the pattern of Fig. 1(c). Whereas Fig. 1(a) has the plane group symmetry $P2$, Fig. 1(c) belongs to $P1$. Each type of atom appears twice in the projection, and from the four coordinates of this pair, all three independent atomic coordinates can be obtained. It is clear that in Fig. 1(b) other directions could have been chosen for the new direction of projection, for example, the diagonal of the A face or the body diagonal.

Similar results can be derived for the other monoclinic space groups (see Black, 1955). The monoclinic cell is effectively replaced by a triclinic cell, which will have a centre of symmetry if the monoclinic space group has one. For example, in $P2/m$ the four symmetry-related atoms (in general positions) would project parallel to an oblique axis to give two independent peaks, since the centre of

symmetry is preserved in the projection. For a non-primitive (monoclinic) lattice, the new axis can be chosen to define either a primitive or a centred triclinic cell.

The discussion can easily be extended to space groups of higher symmetry. Four atoms related by symmetry in an orthorhombic space group may give either two or four independent positions in an oblique projection. Conventional projections which are normal (e.g. in tetragonal or hexagonal) or oblique (e.g. to the triad in a cubic) to symmetry axes give independent peaks for symmetry-related atoms. Oblique projections may still be useful to resolve particular atoms which superpose accidentally in axial projections.

The discussion leads to two main conclusions which may be of use in refining structures by Fourier methods. The first is that in all space groups, except $P1$ and $P\bar{1}$, it is possible in principle to obtain all atom parameters from a single two-dimensional projection. The three-dimensional parameters will be obtained from linear combination of pairs of parameters measured in the projection (Fig. 1), so that the standard errors in them will be of the order of $\sqrt{2}$ times the normal standard error. In some cases, more than one value of each parameter is obtained because there may be more than two related atoms in the asymmetric unit; then the standard error will be reduced. Where it can be applied, the method should be more accurate and less laborious than the use of higher-layer syntheses (Cochran & Dyer, 1952).

The second conclusion is that, in a complex structure, several possible projections can be considered for refinement, and it may be possible to resolve all atomic peaks clearly by using a few selected projections and so avoid the necessity for three-dimensional refinement. Each projection requires data for only one zone which can be collected on zero-layer oscillation or Weissenberg photographs, so avoiding the uncertainties introduced by distortion of spot shapes and inter-layer correlation factors. Even in three-dimensional work, one might (for example) choose an oblique direction for a bounded pro-

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