l'influence de l'ordre de grandeur de l'angle de Bragg, ce qui nous permettra de savoir dans quelles limites l'approximation de 'colonne' (cas limite pour lequel l'angle de Bragg est nul) reste acceptable.

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The Determination of Accurate Unit-cell Dimensions from Inclined Weissenberg Photographs

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The method of Main and Woolfson for obtaining accurate unit-cell dimensions from ordinary zero-layer Weissenberg photographs is extended to general (including equi-inclination) upper-layer Weissenberg and oscillation photographs.

Introduction

Main & Woolfson (1963) showed that accurate unit-cell dimensions could be obtained from the separations of the $\alpha_1 - \alpha_2$ doublets on ordinary zero-layer Weissenberg photographs. The results are insensitive to errors in the camera radius and the same photographs are used for the intensity measurements and the determination of unit-cell dimensions; thus the method is particularly appropriate to low temperature studies. However when a crystal is grown *in situ* it is sometimes possible to obtain good photographs only about a single oscillation axis, with the result that not all the unit-cell dimensions can be determined from the single zero-layer photograph. Hence we have extended the technique to upper-layer photographs.

Theory

The basis of our method is the determination of $\sin^2\theta$ from the α doublet separation t on the film at right angles to the oscillation axis direction. The unit-cell dimensions are then calculated analytically and their standard deviations estimated statistically. Main & Woolfson determined $\sin\theta$, which required a least-squares iteration starting with approximate values of the cell constants.

For the zero-layers, instead of the approximation proposed by Main & Woolfson, we use the corresponding exact expression:

$$\sin^2\theta = \{1 + [(\delta\lambda/\lambda \sin \delta\theta) + \tan(\delta\theta/2)]^2\}^{-1} \qquad (1)$$

where $\delta\theta = t/2r$, r is the camera radius, λ is the α_1 wavelength and $\delta\lambda$ the difference in α_1 and α_2 wavelengths.

For the upper layers it is necessary to know the value of the real unit-cell length a appropriate to the oscillation axis in order to calculate $\sin^2\theta$. In practice we begin with the approximation $\delta\theta = t \cos \mu/2r$ where $-\mu$ is the camera inclination angle (see below); this effectively assumes equi-inclination for both α_1 and α_2, and that $\sin^2\theta$ approaches unity. Hence, *via* (1) and the route outlined in the following section, an approximate value of a is found and substituted in the exact expression (below) for $\sin^2\theta$. This leads to a better approximation for a, which is resubstituted in the exact expression for $\sin^2\theta$, *etc.* This procedure is found to converge in three or four cycles.

Consider the stereographic projection shown in Fig. 1. The symbols (and signs thereof) are the same as in *International Tables for X-ray Crystallography* (1959), which is also the source for (7) below. Note that some authors give the opposite sign for μ. I is the incident

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beam, D the diffracted beam, U the undeviated beam and Q the oscillation axis. From the spherical triangle UDQ,

$$\cos 2\theta = \cos(90+\mu)\cos(90+\nu) + \sin(90+\mu)\sin(90+\nu)\cos\gamma\,,$$

which on rearrangement gives:

$$\cos\gamma = (1-2\sin^2\theta - \sin\mu\sin\nu)/\cos\mu\cos\nu\,. \qquad (2)$$

This expression may also be obtained from that in *International Tables* by substitution for ξ and ζ. If we use the subscript 1 for α_1 and 2 for α_2 radiation, it follows from Bragg's law that:

$$\sin^2\theta_2 = \sin^2\theta_1(1+\delta\lambda/\lambda)^2\,; \qquad (3)$$

thus from (2) for α_2 radiation,

$$\cos(\gamma+\delta\gamma) = \frac{[1-2\sin^2\theta_1(1+\delta\lambda/\lambda)^2 - \sin\mu\sin\nu_2]}{\cos\mu\cos\nu_2}\,, \qquad (4)$$

where $\delta\gamma = t/r$. Expanding $\cos(\gamma+\delta\gamma)$ in (4), substituting for $\sin^2\theta_1$ from (2), and rearranging, we have

$$\cos\gamma[\cos(\delta\gamma) - (1+\delta\lambda/\lambda)^2\cos\nu_1/\cos\nu_2] - \sin\gamma\sin(\delta\gamma) = \frac{1-\sin\mu\sin\nu_2 - (1+\delta\lambda/\lambda)^2(1-\sin\mu\sin\nu_1)}{\cos\mu\cos\nu_2}\,;$$

hence

$$\cos(\gamma+\tau) = \frac{1-\sin\mu\sin\nu_2-(1+\delta\lambda/\lambda)^2(1-\sin\mu\sin\nu_1)}{\cos\mu\cos\nu_2\{\sin^2\delta\gamma + [\cos(\delta\gamma)-(1+\delta\lambda/\lambda)^2\cos\nu_1/\cos\nu_2]^2\}^{\frac{1}{2}}}\,, \qquad (5)$$

where

$$\tan(\tau) = \sin(\delta\gamma)/[\cos(\delta\gamma) - (1+\delta\lambda/\lambda)^2\cos\nu_1/\cos\nu_2]\,. \qquad (6)$$

But since

$$\sin\nu_1 = \sin\mu + n\lambda/a\,, \qquad (7)$$

where n is the value of the index h, k or l appropriate to the oscillation axis, and a the relevant real unit-cell length,

$$\sin\nu_2 = \sin\mu + n(\lambda+\delta\lambda)/a\,. \qquad (8)$$

Hence from (5), (6), (7) and (8) γ can be calculated and substituted in (2) to obtain $\sin^2\theta_1$.

Calculation of unit-cell dimensions

The expressions:

$$\sin^2\theta = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk$$

are a system of linear equations with known coefficients. As shown in *International Tables*, they may be solved analytically *via* inversion of the matrix of normal equations set up by minimizing $\Sigma\, w_i\delta_i^2$, where w_i is the weight of the ith reflexion and δ_i the difference between the observed and calculated values of $\sin^2\theta_i$. An analytical weighting scheme for non-zero-layers would be extremely complicated, so we vary t by a small increment and calculate the resultant change in $\sin^2\theta$. The weights are set equal to $\delta t/\delta(\sin^2\theta)$, which assumes that the expected error in measurement of t is proportional to $t^{\frac{1}{2}}$. The real unit-cell dimensions are then determined in the usual way from the analytical constants $A\cdots F$.

Estimation of standard deviations

As shown in *International Tables* the standard deviations are calculated from the diagonal elements b^{rr} of the inverse matrix of normal equations. However the assumption that the distribution of the residuals δ_i is normal is invalid in this particular problem, owing to the nature of the weighting scheme adopted; this leads to standard deviations which are too low. Hence we replace the term $(N-K)$ by $[(\Sigma\, w_i)^2/\Sigma\, w_i^2]-K$, where N is the number of reflexions and K the number of analytical constants which can be determined. This behaves correctly in the limiting cases of $w_j = w_{i\neq j}$ and $w_j = 1$, $w_{i\neq j} = 0$. The expression for the standard deviation in the analytical constant u_r is then:

$$\sigma_r = \{(b^{rr}\,\Sigma\, w_i\delta_i^2)\}/\{[(\Sigma\, w_i)^2/\Sigma\, w_i^2)]-K\}^{\frac{1}{2}}\,. \qquad (9)$$

If the denominator is less than unity the unit-cell is ill-defined. The estimated standard deviation in a real unit-cell dimension is found by taking the square root of the sum of the squares of the changes in its value caused by varying each analytical constant in turn by its estimated standard deviation.

Performing the calculations

A program has been written for the Cambridge University Titan computer which enables the above calculations to be carried out for all seven crystal systems. The input data consist of crystal system code number, $\lambda\alpha_1$, $\delta\lambda$ and r; followed by blocks of any number of h,k,l,t sets. Each block is headed by the oscillation axis code number and inclination angle $(-\mu)$, there being one such block per photograph. Hence data about 1, 2 or 3 axes may be included. The output includes simple tests on the denominator of (9) to show whether the standard deviations are reliable. If one or more analytical or real unit-cell constants are indeterminate, they are printed as zero and matrix singularities avoided, so that the rest of the output is correct. The program takes about 15 seconds for a six-cycle refinement with 40 reflexions.

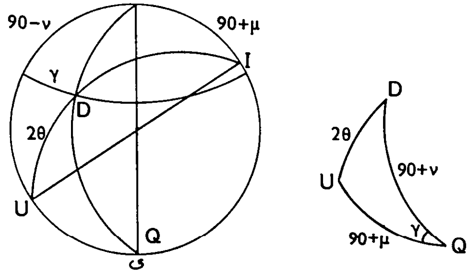

Fig. 1. Stereographic projection.

Results

The technique has been tested on several compounds with satisfactory results, as shown in Table 1.

(i) *Pentakisdiethylphenylphosphine diruthenium tetrachloride* (PPRTC), *monoclinic.* Data for layers *hk*0 to *hk*8 ($\mu = -35{\cdot}5°$) gave cell constants in agreement with those determined by a least-squares fit to data from an internally calibrated Guinier photograph (Alcock & Raspin, 1957). All the standard deviations were satisfactory, ranging from 0·2% to 0·09%. The estimated standard deviations from the powder data shown in Table 1 are double those from the least-squares fit to allow for possible systematic errors.

(ii) *Aenigmatite, triclinic.* Data for *hk*0, *hk*1, 0*kl* and *h*0*l* gave unit-cell dimensions in agreement with those found from back-reflexion oscillation and precession photographs by Kelsey & McKie (1964). The two methods yielded similar standard deviations, the $\alpha_1 - \alpha_2$ method with appreciably less effort.

(iii) *Nyererite, orthorhombic.* Data for *hk*0 to *hk*5 ($\mu = -17{\cdot}7°$) gave good values for *a* and *b* in agreement with those found by McKie (1966) from back-reflexion photographs. However, although the two *c* values were in good agreement, that from the $\alpha_1 - \alpha_2$ splittings had a standard deviation of 2½%. This demonstrates that well defined analytical constants *C*, *D* and *E* may be determined from [001] oscillation-axis data alone only if a wide range of values of μ is used. Our experience with other crystals confirms this.

(iv) On testing the program on the original zero-layer data of Main & Woolfson for thallium hydrogen tartrate, not only were the calculated unit-cell dimensions in agreement to six significant figures, fully justifying any minor approximations in either treatment, but the estimated standard deviations were within ten per cent of each other, despite the fact that theirs were derived from an estimated error in the measurement of the $\alpha_1 - \alpha_2$ splittings, and ours were estimated statistically by the normal least-squares procedure.

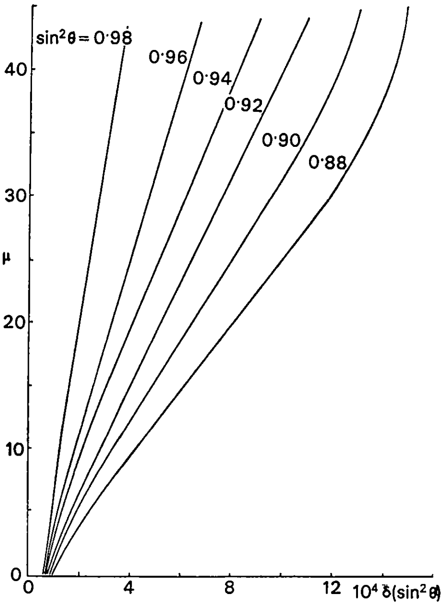

Fig. 2. Errors in $\sin^2\theta$ for $\delta\mu = -0{\cdot}5°$.

Possible systematic errors

If the crystal is slightly misset by an angle δm, the crystallographic zone axis will precess about the oscillation axis, and the errors in the splittings will be of the same order as when μ has errors ranging from $+\delta m$ to $-\delta m$. This has been investigated by calculating the expected α doublet separations *t* for various $\sin^2\theta$ values and $\mu = \mu_0 - \delta\mu$, and then using these and $\mu = \mu_0$ to recalculate the $\sin^2\theta$ values and so find the error in $\sin^2\theta$ corresponding to a given error $\delta\mu$ in μ. The value of *a* was the same in both calculations and chosen so that $-\mu_0$ was the α_1 equi-inclination angle. The results are linearly dependent on $\delta\mu$ in the range $-0{\cdot}5° < \delta\mu < +0{\cdot}5°$; those for $\delta\mu = -0{\cdot}5°$ are shown in Fig. 2. The effect is small compared with random errors in $\sin^2\theta$,

Table 1. *Comparison of unit-cell dimensions found for three compounds with data obtained by alternative methods*

	PPRTC		Aenigmatite		Nyererite	
	$\alpha_1\alpha_2$	Guinier	$\alpha_1\alpha_2$	Precession and back-reflexion	$\alpha_1\alpha_2$	Back-reflexion
a	15·882 Å ±0·013	15·883 Å ±0·009	10·414 Å ±0·019	10·406 Å ±0·013	25·250 Å ±0·027	25·21 Å
b	19·078 ±0·017	19·094 ±0·007	10·833 ±0·019	10·813 ±0·014	8·816 ±0·012	8·81
c	10·418 ±0·018	10·406 ±0·005	8·930 ±0·008	8·926 ±0·006	12·73 ±0·29	12·74
α	90°	90°	105·10° ±0·12	104·93° ±0·15	90°	90°
β	104·18 ±0·07	104·06 ±0·05	96·65 ±0·14	96·87 ±0·18	90	90
γ	90	90	125·39 ±0·11	125·32 ±0·10	90	90
N	58		73		23	
R	0·0034		0·0024		0·0026	

N = number of reflexions
$R = \Sigma w_i \delta_i^2 / \Sigma w_i$

reaching a maximum for $\mu=-45°$ and $\sin^2\theta=0{\cdot}86$ of only 0·0015. Since this is in every respect an extreme case, errors due to crystal missetting may be safely ignored. This relative insensitivity to the value of μ also explains why the program converges rapidly in a.

The method is very insensitive to the camera radius. A change of 1% in the value used for the aenigmatite data produced only a change of 0·03% in the calculated unit-cell dimensions.

Conclusions

This extension of Main & Woolfson's technique has the advantages that only data about a single axis are required, and that (even when data from several axes are available) more information can be incorporated. It can also be recommended as a quick and highly effective check that a set of upper-layer Weissenberg photographs have been consistently indexed, since an incorrectly indexed reflexion is immediately apparent on comparing the $\sin^2\theta$ values from the α doublet separations with those calculated from the analytical constants.

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Diffuse Double Diffraction of X-Rays

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A Monte Carlo method has been used to evaluate the magnitude of twice scattered X-rays in diffraction experiments. The quantitative effects of variations in the primary scattering distribution, the absorption coefficient, the scattering power of the atoms, the X-ray wavelength, the specimen thickness, the monochromator and slit configuration and of polarization corrections have been derived. These factors have various influences on the magnitude and angular distribution of the twice scattered radiation but $I_2(\theta)$ is of the order of $0{\cdot}0025\ \sigma^2/\mu_\rho W$ (electron units per atom) for all the elements and conditions considered, where σ^2 is the square of the primary diffraction cross-section, μ is the mass absorption coefficient and W is the atomic weight.

The experimental measurements of diffusely scattered radiation include contributions due to multiply scattered radiation. Often, this contribution must be accounted for in order to analyse the coherently diffracted component. Chandrasekhar (1950) has derived certain expressions for the multiple scattering of radiation but these are not directly applicable to most diffraction experiments. Vineyard (1954) has obtained expressions for the doubly scattered component of neutron radiation, with isotropic primary scattering $[I_1(\theta)]$ and two common diffraction geometries. Warren (1959*a*) has obtained numerical values for the double scattering of Cu $K\alpha$ X-radiation from a polycrystalline sample of copper in the normal Bragg–Brentano X-ray reflection geometry, representing the primary scattering as a finite sum of sharp reflections. The conditions assumed in either of these two calculations would not appear to be applicable to liquid or amorphous specimens. With such materials $I_1(\theta)$ is not isotropic nor does it consist of a few sharp reflections. In addition, if absorption in the sample is low, and if the incident and detected beams are restricted (as they are by slits or monochromators) the geometrical conditions may be abnormal.

In this paper we present the results of more general Monto Carlo calculations. The quantitative effects on the double scattering of variations in the primary scattering distribution, the absorption coefficient, the scattering power of the atoms, the specimen thickness, the monochromator configuration and of polarization corrections are shown. We consider only the double scattering of X-rays from the 'surface' of a flat sample large enough to intercept the entire beam, with source and detector situated symmetrically with respect to the surface normal.

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