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A simple precision method for the determination of cell parameters.

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As all X-ray methods for determining reciprocal-vector lengths are based on Bragg's law,

$$\mathbf{s}-\mathbf{s}_0=\boldsymbol{\sigma},\ |\mathbf{s}|=|\mathbf{s}_0|=1,\ |\boldsymbol{\sigma}|=2\sin\theta=n\lambda/d\ , \qquad (1)$$

there are three and only three X-ray goniometric possibilities for finding $|\boldsymbol{\sigma}|=\sigma$:

1. '$\mathbf{s}-\mathbf{s}_0$ methods', implying a study of the angle $\angle(\mathbf{s}, \mathbf{s}_0)$. Instances are several well-known methods where the incident beam—direction of $\mathbf{s}_0$—is mechanically defined and the reflexion direction, or directions, are studied.

2. '$\mathbf{s}-\boldsymbol{\sigma}$ methods'. The earliest example is the use of the tube spectrometer (Siegbahn & Leide (1919), Larsson (1927)), where crystal turning was measured in relation to an (almost) fixed reflexion direction.

3. '$\mathbf{s}_0-\boldsymbol{\sigma}$ methods'. The first example is due to DuMond (1947), who described an apparatus for determination of γ ray wavelengths, measuring sample positions in relation to diffracting crystal at maximum reflexion intensity.

Now, of the directions implied by (1), the direction of $\mathbf{s}_0$ can be defined with great precision. The direction of $\boldsymbol{\sigma}$ is for a perfect crystal defined by the orientation of the crystal and can then be measured with an exactness dependent only on workshop skill. For a mosaic crystal the exactness is more or less decreased. The direction of $\mathbf{s}$, finally, is associated with practically all those problems that have been discussed in the literature in connection with precision methods: sample and film eccentricity, film shrinkage etc. A still more fundamental problem associated with $\mathbf{s}$ is that, if focusing of the X-rays occurs in front of the crystal, there is an unavoidable line or spot width for any finite, unbent crystal with a finite absorption.

For comparison it can be mentioned that the angular precision attainable for the direction of $\boldsymbol{\sigma}$, namely *ca.* 0·2″ (Larsson (1927), Olof Beckman, private communication) would, for the same precision in the direction of $\mathbf{s}$, correspond to an uncertainty in line or spot position —on a film with *ca.* 10 cm. radius—of *ca.* 0·0001 mm.

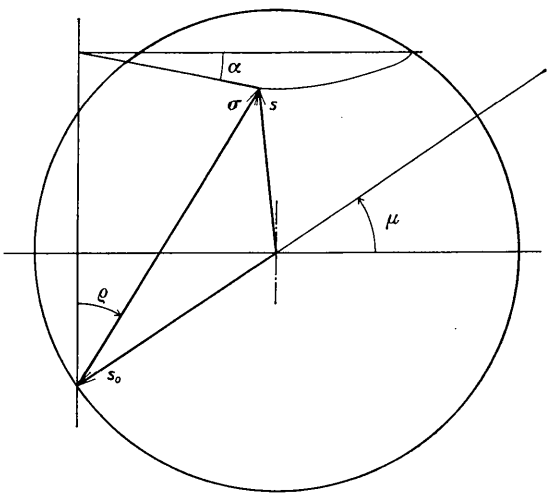

Fig. 1.

The logical consequence is that for good, unbent crystals, $\mathbf{s}_0-\boldsymbol{\sigma}$ methods offer the prospect of being capable of a precision several orders of magnitude better than any standard method using the $\mathbf{s}$ direction.

Using a general inclination (see Fig. 1) one finds

$$\sigma=2\{\sin\mu.\cos\varrho+\cos\alpha.\cos\mu.\sin\varrho\}\ . \qquad (2)$$

In order to find the theoretically best method to determine σ, we now study $\Delta\sigma$ for small errors $\Delta\alpha$, $\Delta\mu$, $\Delta\varrho$. Under these conditions equation (2) yields

$$\begin{aligned}\Delta\sigma=&-2\sin\alpha.\cos\mu.\sin\varrho.\Delta\alpha\\&+2\{\cos\mu.\cos\varrho-\cos\alpha.\sin\mu.\sin\varrho\}.\Delta\mu\\&+2\{-\sin\mu.\sin\varrho+\cos\alpha.\cos\mu.\cos\varrho\}.\Delta\varrho\ ,\end{aligned} \qquad (3)$$

from which it follows that small errors in α, μ or ϱ will cause no error in σ for $\mu+\varrho=90°$, $\alpha=0$, and only small, second-order errors for $\mu+\varrho\approx 90°$ and $\alpha\approx 0°$.

If $\mu+\varrho=90°$ is chosen, then, for any α (and small differences):

$$\Delta\sigma=(1-\cos\alpha).\sin 2\mu.(\Delta\mu-\Delta\varrho)-2\sin\alpha.\cos^2\mu.\Delta\alpha\ . \qquad (4)$$

For the rest of this paper we shall discuss only the case $\mu=0°$, $\varrho=90°$ ($\alpha=90°-\theta$), thus eliminating small errors in μ and ϱ. (The favourable case $\mu\approx 90°$ is unobtainable with standard Weissenberg apparatus.) (2) and (4) now yield:

$$\sigma=2\cos\alpha \qquad (2')$$

$$\Delta\sigma=-2\sin\alpha.\Delta\alpha \qquad (4')$$

i.e.

$$\Delta d/d=\tan\alpha.\Delta\alpha=-\cot\theta.\Delta\theta\ . \qquad (5)$$

In this technique we can thus, for accurate adjustments, eliminate errors in μ and ϱ, and the method suffers only from errors in α. Systematic errors in α would also be eliminated (for a finite $\Delta\alpha$) if appropriate extrapolation is made to $\alpha=0°$ ($\theta=90°$) (see below).

If $\mathbf{s}_0$ is to be defined by the crystal in connection with a small but finite pinhole, the most important source of error, is the diffusion of incident radiation. A theoretical study of this error is very intricate (existing formulae for 'absorption error' do not apply to the present method). Empirical extrapolation functions therefore have to be used.

These arguments led the author in 1956 to try out the method of finding $|\boldsymbol{\sigma}|$ for zero-zone reciprocal vectors, using a commercial Weissenberg goniometer equipped with an angular vernier. For better definition of $\mathbf{s}_0$, the pinhole system was replaced by a shorter one with a hole diameter of 0·15 mm., thus decreasing the diffusion of the incident beam. From a traditional Weissenberg photograph, the two ω values ($\Delta\omega=2\alpha$) were approximately located. With the layer-line screen inserted, a series of film exposures (fixed film cylinder appro-

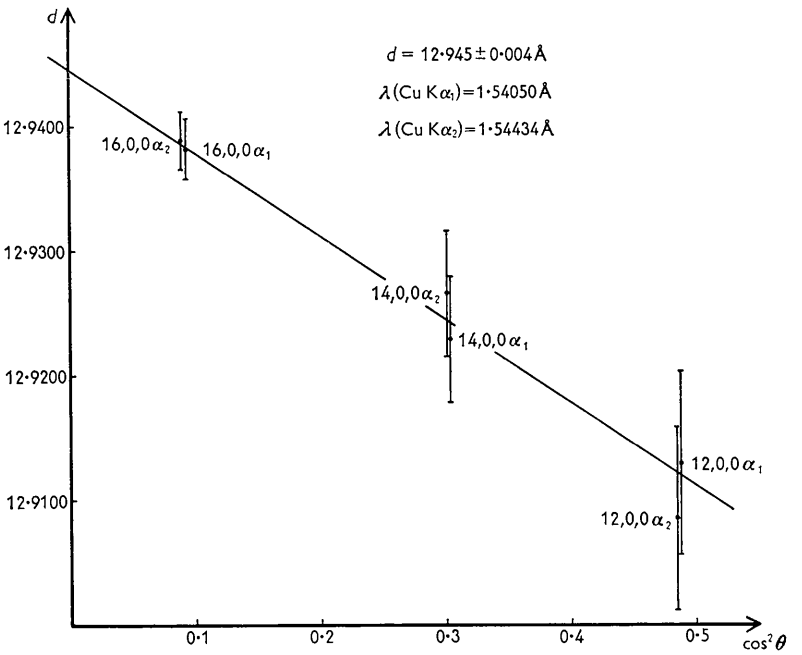

Fig. 2.

priately translated between successive exposures) were made with stationary crystal every 10′ about the two expected ω values. The positions for maximum intensity were interpolated from visual film-intensity estimates. (The reproducibility was about $\pm 2'$ or less for a reasonably large experience of reproducibility, which would correspond to $\pm 1/30$ mm. on the film for the apparatus used.)

The results for appropriate vectors defined by the set of planes studied were then plotted *versus* different trial functions of θ. It was found that the standard extrapolation function $\cos^2\theta$ (see e.g. Buerger (1942–9), Chapter 20) was reasonable. Fig. 2 gives an example ($FeCl_3$ 2·5 H_2O). The limits correspond to $\Delta\alpha = \pm 2'$. They do not include any systematic errors, but correspond to estimated maximum random errors.

In so far as the extrapolation technique is justifiable for all systematic errors, the accuracy in extrapolated value is almost as high as the reproducibility in the d value corresponding to the lowest $\cos^2\theta$, especially if this is very low. The wavelength should therefore if possible be chosen with respect to the extreme vector (vector length as near as possible, but not exceeding, 2 units, cf. equations (2′) and (4′).

The accuracy—or at least reproducibility—is extremely good, considering the experimental equipment. Since the method was first used at this Institute* it has developed into a routine procedure (Lindqvist & Mörtsell (1957), Hermodsson & Strandberg (1957), Lindqvist & Brändén (1959) and others) and is recommended for use when high precision is desired.

That the $s_0 - \sigma$ method with good instruments would be capable of giving an accuracy superior to that of any other method was clear from Bond's (1959) report at the Stockholm Conferences.

For oblique cells the reciprocal interaxial angle, in the reciprocal plane studied, can be found either (most simply) from the ω values found for the reciprocal axes (Weisz *et al.*, 1948, § 2) or (more exactly) by triangulation (Buerger, 1942–9, p. 373).

* Compare Weisz *et al.* (1948), who did not, however, use the back-reflexion technique, nor any extrapolation method. These authors seem not to have realized the potentialities of the method.

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