set at the approximate angle, the reflection found and then the tubes were repositioned to give the highest counting rate. Tests show that displacing the counting tubes by 0·8° from the 79·3° position changes the peak R by $2-\frac{1}{2}$ sec. However we will go to scintillation counters when we can get small enough ones. We then count for a fixed time, generally 20 sec., increase R by 20 sec. of arc and count for 20 sec., etc. Generally we do not correct for Geiger tube dead time because this does not shift the peak although it flattens it. If we join successive points by straight lines and then form a curve from the points midway between these points and the opposite connecting lines (at the same intensity level) we find that this derived curve is nearly straight. It cuts the profile at a point we shall call 'the midchord peak.'

A calibration supplied with the clinometer shows irregular errors as high as 5 sec., with a symmetry plane near a reading of 50°. Hence to minimize errors we make 50° the midpoint between the first pair of curves. This is done by turning the crystal carrying shaft in its hole in the clinometer shaft and relocking it. We then repeat with $50°+90°$ as a midpoint, etc., giving four pairs of curves distributed evenly about the circle. As a test case we take silicon as shown in Table 1.

(The temperature correction was made using the expansion coefficient $2{\cdot}33\times10^{-6}$ per deg.cent. This is the value found by D. Gibbons of Bell Labs. by an interferometer method (Gibbons, 1958).)

Discussion

If we weight these three values proportionally to $\tan\theta$/s.d. we get 5·4197695 kXU. The most reliable of the three measurements, the (444), differs from this by less than a part in a million while the worst differs by less than four parts in a million.

The peak widths are roughly correct for a primary beam width of 0·8 min. at half max plus a 'wavelength spread' $300\times10^{-6}\tan\theta$.

In computing the standard deviations we have treated the systematic but compensating errors as random. This should be conservative.

This instrument can be used to measure directional affects such as a comparison of d_{100} in the growing direction of a cubic crystal with d_{010} perpendicular to the growing direction. We have used crystals but little over 1 mm. square and also crystals half an inch in diameter.

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International Union of Crystallography

Conference in Stockholm, 9-12 June 1959

The Precision Determination of Lattice Parameters

As has been reported in *Acta Cryst.*, **12**, 1054–1055 (1959), the Commission on Crystallographic Apparatus held a very successful series of conferences in Stockholm during the period 9–12 June 1959. It had been arranged that the papers presented at the Conference on Precision Lattice-Parameter Determination would be published as a group in *Acta Crystallographica*. However, about half of the speakers have not provided manuscripts for publication, and the eight papers printed below are all that are availabe in the form in which they were presented. They have been prepared for publication by the Chairman of the Commission on Crystallographic Apparatus (Dr W. Parrish), and the Editors of *Acta Crystallographica* are grateful for his help. One other paper appeared in expanded form (p. 814).

The final report of the Commission on its lattice-parameter project is published on p. 838 of this issue.

Acta Cryst. (1960). **13**, 818

Some sources of error in precision determination of lattice parameters.

By M. E. Straumanis, *Department of Metallurgical Engineering, University of Missouri School of Mines and Metallurgy, Rolla, Missouri, U.S.A.*

(*Received* 11 *June* 1959 *and in revised form* 12 *January* 1960)

The absorption correction

The displacement of Debye–Scherrer lines as well as of reflections of a single rotating crystal due to absorption of the X-ray beam by the sample follows from a simple geometry. Hadding (1921) derived an expression for the correction $\Delta\theta$ of the Bragg angle θ assuming that the sample was completely opaque:

$$\Delta\theta = fr\cos^2\theta\,, \qquad (1)$$

where r is the radius of the sample in *mm* and f a factor converting *mm* into degrees. The same equation was also derived and discussed later by Buerger (1942). By means of equation (1), $\Delta\theta$ of a line can be calculated and subtracted from the Bragg angle measured. As this calculation is only approximate (the true absorption of a sample is difficult to compute), other ways for the elimination of $\Delta\theta$ were considered.

One of the most successful methods was proposed by Taylor & Sinclair (1945) and independently by Nelson & Riley (1945). Now, it is interesting to plot against their ξ-function not the lattice constants as measured, but those as calculated for a certain substance, assuming that the absorption shifts the lines according to equation (1). The substance itself is not important, because complete absorption is assumed, but only the radius of the sample. In Fig. 1 such a a–ξ plot for aluminum is given.

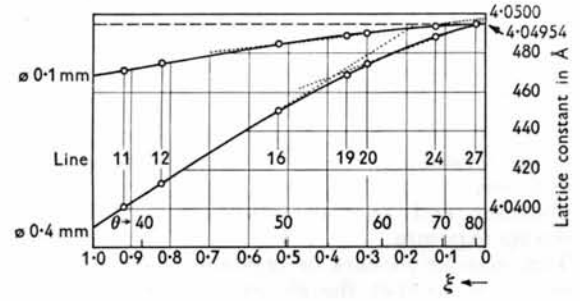

Fig. 1. Theoretical a–ξ plot for Al. The constant $a = 4{\cdot}04954$ Å (not corrected for refraction) was distorted by subtracting amounts, calculated from equation (1) and the Bragg equation for various θ angles. Cu-radiation. Dotted lines lead to extrapolated values of lattice constants.

Fig. 1 shows clearly the dependence of the lattice constants on the diameter of the samples and on the reflection angle: Having thin samples (about 0·1 mm. in diameter) the constants tend to level out at high θ-angles. Comparing Fig. 1 with the curve obtained in real measurements, Fig. 2, the similarity of both curves becomes obvious. Thus, it can be concluded, absorption corresponds closely to the geometrical mechanism proposed by Hadding.

The uncertainty of the straight line extrapolation using the a–ξ plot can clearly be seen from Fig. 1 (dotted lines): The extrapolated value of the constant depends upon the diameter of the sample and is larger than the initial one. The only way to recover the original constant (4·04954 Å) is to draw a parallel to the abscissa through the last point (Fig. 1, dashed line). The uncertainty of extrapolation is greater in cases of actual measurement, because of increased scatter of the experimental points. The ambiguity in lattice constants can be eliminated by the use of very thin and semitransparent powder mounts (below 0·2 mm. in diameter). In such cases the a–ξ curve levels out at high Bragg angles and the most reliable constant is calculated from the *last sharp* or *strong interference* (θ above 70°). Because of the vanishing absorption shift no correction except that for refraction is then necessary (Straumanis, 1955, 1956). To calculate the precision of determination, several patterns of the substance should be made and measured. The constants calculated from lower reflection angles are meaningless for the whole determination. This solution (Straumanis & Mellis, 1935; Straumanis & Ieviņš, 1936, 1959) was found 10 years before the publication of the Taylor–Sinclair and Nelson–Riley extrapolation method.

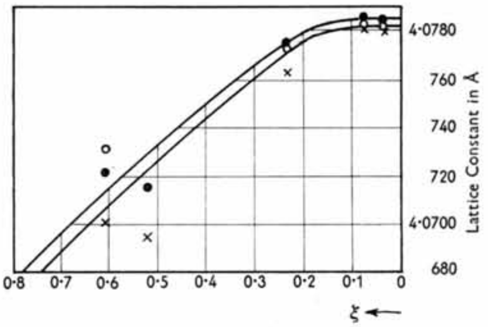

Fig. 2. a–ξ plot for Au powder. Diameter of the sample about 0·20 mm. Co-radiation. The upper curve is obtained from the lower by addition of the refraction correction.

The 2θ angle

The usual procedure is to measure on the film the small 4Φ angles. However, there are methods which measure only the 2θ angle. It is evident that such methods have a lower precision by at least a factor of two, and also there is an additional error involved by a possible non uniform radiation intensity distribution within the primary beam. The spots of the upper row of Fig. 3 were obtained by irradiating a film, which was placed about 7 cm. from the end of the 1 mm. aperture, by the primary X-ray beam for a fraction of a second. It can be seen clearly that the intensity is not uniformly distributed in the beam, although efforts were made to get a spot of even intensity on the screen. The same is obtained with

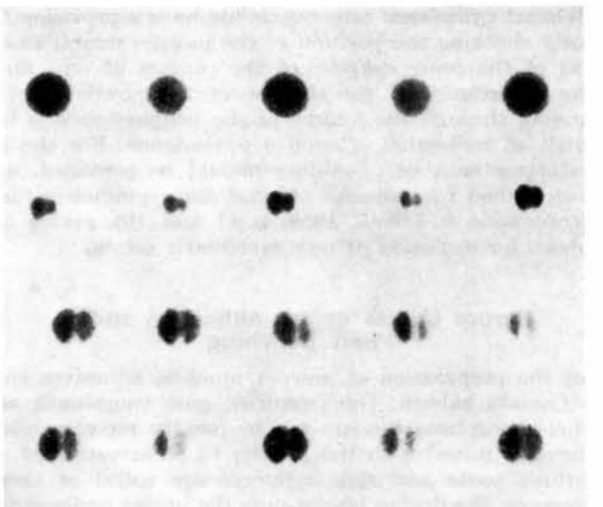

Fig. 3. Spots produced by the primary beam of a powder camera on a film.

Top row: 1 mm. aperture.
2nd row: 0·5 mm. aperture, powder mount (W) 0·12 mm. in diameter in the camera.
3rd and 4th rows: 1 mm. aperture, the same mount.

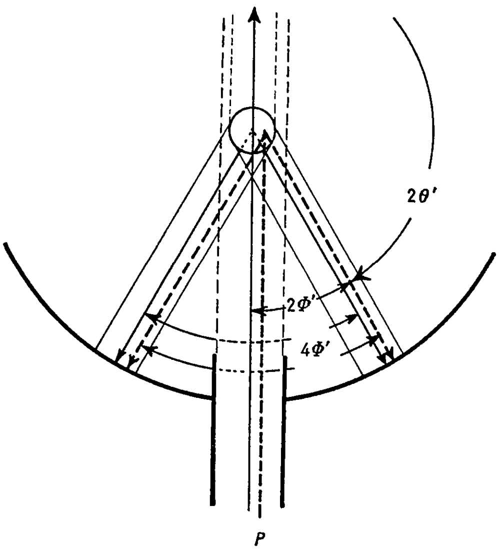

Fig. 4. Error involved in $2\theta'$ or $2\Phi'$ measurement due to non uniform intensity distribution in the primary beam P.

a powder mount in the center of the camera. Hence, the mount in case of Fig. 3 is not uniformly irradiated, and this causes a shift of the peak intensity of the diffraction lines (Fig. 4), especially when the mount is thicker. While this effect is averaged out by all methods measuring 4Φ or 4θ, it may cause an appreciable error if only 2θ is determined (see Fig. 4). Thus, using the 2θ methods, the uniformity of the X-ray beam and the position of the sample (it should go exactly through the diameter of the beam) must be checked.

Sample in the cylinder axis

All exact cylindrical cameras should have a provision for easily checking the position of the powder mount *in the axis* of the *inner cylinder* of the camera at any time. The appearance of the shadow of the powder mount running through the middle of the primary spot is not at all an indication of such a coincidence. For the investigator another possibility should be provided, e.g. as described for cameras adapted for asymmetric films (Straumanis & Ieviņš, 1959, p. 11 and 19), giving the chance for exclusion of new systematic errors.

Errors due to drying adhesives and to hole punching

For the preparation of powder mounts, adhesives such as Canada balsam, Duco cement, gum tragacanth and other amorphous binders are frequently recommended. They are mixed with the powder to be investigated, to a thick paste and thin cylinders are rolled of them. However, the drying binder puts the grains under strain and even deforms them; this effect may be accompanied, although not yet proved, by a change in lattice parameter* and an increase in the line breadth. The best way to avoid these changes and, simultaneously, to make the specimen semitransparent to X-rays is to stick the powder to a thin Lindemann glass fiber (about 0·08 mm. in diameter), coated with a thin layer of a non-drying adhesive (Straumanis & Ieviņš, 1959, p. 30–35).

It has been shown that a large shrinkage of the film occurs around the hole punched through it (Jellinek, 1949). In precision films the last back reflection interferences are close to the hole and the rings may become uncontrollably displaced due to non uniform shrinkage of the film around this hole after development. The danger of obtaining erroneous lattice constants increases with lines at high Bragg angles (Straumanis & Weng, 1956). Therefore, the holes in precision films should never be punched but carefully drilled with sharp circular steel drill bits (see Azároff & Buerger, 1958).

Conclusion

A precision up to 1:200,000 and better (depending upon the sharpness, intensity and position of the last lines) can be attained under the following conditions in the measurement of lattice parameters using for comparison the averages of two or more determinations:

1. Precisely built cameras with the powder mount or single crystal exactly in the axis of the inner camera cylinder.
2. Constant and known temperature of the sample during exposure.
3. Thin powder mounts or crystals (below 0·2 mm. in diameter) so that the absorption correction can be disregarded for lines at high Bragg angles.
4. The grains of the powder should not be deformed and the holes in the films should be carefully drilled (not punched).
5. The 4Φ and not the 4θ or even 2θ angles (on symmetric films) should be measured (using the density maxima of the lines).

The precision obtained under such conditions pertains to the *reproducibility* of the constants but not to their absolute value (because e.g. of the uncertainty of wavelengths).

Summary

When using very thin single crystals or powder mounts (~ 0·12 to 0·17 mm. in diameter), the absorption shift of lines at high Bragg angles is vanishing, as the curves of the a–θ or of a–ξ (Taylor–Nelson–Riley) plots level out in that region. Generally the experimental curves agree with the calculated ones, if the Hadding geometry of line displacement due to absorption is adopted. If, instead of the 4Φ angles on asymmetric films, the 2θ on symmetric ones are measured, additional errors, due to not uniform intensity distribution within the primary X-ray beam, may be introduced. Provisions should be made in building cameras so that the position of the sample in *the axis* of the *inner cylinder* can be inspected at any time. In preparing powder mounts non-drying glues should be used. The holes in the films should be carefully drilled (not punched).

The present investigation was sponsored by the National Science Foundation under the contract G 2585. Thanks are expressed to Mr T. Ejima and Mr H. W. Li for work with the X-ray films.

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* Dr. P. Perio, Saclay (France) states in a recent letter to the author that e.g. the *c*-constant of ZnO is influenced by 3 to 4×10^{-4} Å by the action of the glue. This is a fairly large effect.

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Acta Cryst. (1960). **13**, 821

Discussion of error in lattice-parameter measurements.

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(*Received* 10 *June* 1959 *and in revised form* 8 *January* 1960)

Any discussion of errors assumes that the systematic errors can be handled independently of the random errors. The two types of error are fundamentally distinct; the possibilities for their correction are completely different (Gauss, 1821).

The *random errors*, which appear as irregular deviations of the observations from each other, can never be completely suppressed, but they can be satisfactorily calculated by means of an averaging method if there is a sufficient number of observations. From all observed values, a, the mean $\bar{a}$ is derived. Usually the root-mean-square error is used as a measure of the random errors $\pm m$ ('standard deviation', 'mittlerer quadratischer Fehler'). The influences of separate errors add quadratically (law of the propagation of errors). In this averaging procedure, based on the Gaussian least-squares method, the systematic errors are not considered, a fact frequently overlooked in the literature.

The *systematic errors* are additional unidirectional deviations of the observations from the true value, and add linearly. In contrast to the random errors, they can be eliminated in principle, though they are more likely to remain undetected. Their elimination or reduction depends only on the test procedure and evaluation of the experiments, but *not* on a high number of observations. The remaining part Δa of the systematic errors is unknown, but can be detected by independent comparison measurements, as discussed below.

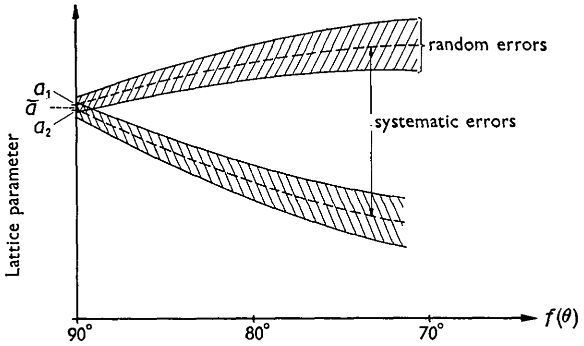

Fig. 1. Random and systematic errors in the extrapolation method (schematic); $\bar{a}$ is the mean value of two exposures with the same measuring method.

For the precise determination of lattice parameters the precision method of Straumanis has led the way (Straumanis & Ieviņš, 1940). By a refined experimental technique the systematic errors could be vastly reduced. But it has become evident that some residual portion Δa of the systematic errors still remains, in spite of careful procedure and evaluation of the experiments. This is to be seen from the fact that for different exposures the positions and the slopes of the extrapolation curves differ slightly (Fig. 1). Subjective errors of observation in measuring line separations are a serious hindrance. This refers to random deviations with the same observer, but especially to the systematic deviations of several observers compared with each other. The difference between the two values of the lattice parameter calculated from the two components of the $K\alpha$ doublet can give an indication of the amount of the observation errors; these cannot, however, be separated with sufficient certainty from the errors caused by the apparatus. The apparatus errors do not all have the same angular dependence; in general, moreover, they appear to an extent that alters from exposure to exposure and is mostly unknown (Parrish & Wilson, 1959; Weyerer, 1957).

The aim of the author's measurements (Weyerer, 1956) was to fix the extrapolation curve in the back-reflexion region as exactly as possible. This was done by multiple irradiation of the same film by two or three X-ray tubes with different target materials.* For measuring the lines a dial-gauge measuring device operating by the coincidence method has proved good.

Though the extrapolated values obtained with these improvements are relatively accurate, there is no guarantee that all systematic errors are really eliminated. That can be proved only by comparing the results of several methods independent of each other (Debye–Scherrer method; back-reflexion methods; focusing methods in cylindrical cameras; diffractometer method) (Weyerer, 1956), all carried out with the same care and experience.

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* In accordance with theory, refraction is much less important for powder specimens than for single crystals.