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Precision Lattice Constant Determination*

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A single crystal method of lattice constant determination is presented in which the several errors are minimized or corrections computed. The apparatus measures the angle between two reflecting positions of the crystal. With nearly perfect crystals the lattice constants can be measured to a few parts in a million.

With the large, highly pure and perfect single crystals now available (zone refined silicon for example) one should be able to measure lattice constants with an accuracy comparable with the accuracy with which wave lengths of X-rays were determined.

Consider the arrangement shown in Fig. 1. Here, with the crystal in the position shown by the stippled rectangle, a beam is diffracted into the upper counting tube. If the crystal is now turned through a small angle into the position shown by the unstippled rectangle, a beam is diffracted into the lower counting tube. One now has a choice: whether to measure the angle between the two counting tube positions, or to measure the angle between the two positions of the crystal.

Eccentricity error

If the crystal, Fig. 1 is off center the beam does not follow the paths shown in Fig. 1 and this causes the beam angles to be read wrong. However, if one uses large windows in the counting tubes the crystal angles with the collimated beam are still correct and can be read accurately.

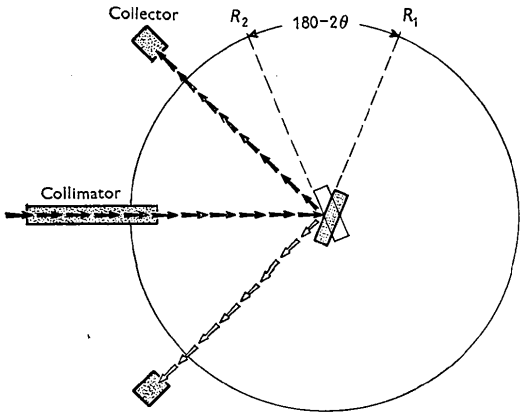

Fig. 1. Measurement system used in this paper.

That the eccentricity error is very effectively removed is easily demonstrated. A one mm. thick crystal has one surface centered, the other, one mm. off center. Both sides give the same θ if θ is large enough that the beam strikes the eccentric surface.

Absorption error

Since absorption merely displaces the beam it affects the apparent beam angle but not the crystal angle at reflection. From this we see that if we measure between the reflected beams both eccentricity and absorption cause errors, while if we measure between crystal positions neither of these causes errors.

Zero error

We note the reading of the crystal position on a divided circle for one position, say R_1, and then note the reading R_2 for the second. It is readily shown that for $R_2 > R_1$ and $R = 0$ not between R_1 and R_2:

$$\theta = 90° - (R_2 - R_1)/2 \,. \qquad (1)$$

If $R = 0$ lies between R_1 and R_2 one will need to modify this equation to:

$$\theta = (R_2 - R_1)/2 - 90 \,. \qquad (1')$$

This method of determining θ eliminates the zero error.

Crystal tilt error

One must be sure that the atomic plane being used is sufficiently parallel to the axis of rotation. In Fig. 2 let x be the axis of rotation and N the normal to an atomic plane which lacks perpendicularity to axis x by amount Δ. The measured Bragg angle is θ' but this is not the true Bragg angle. Simple analysis gives us the relation:

$$\sin\theta = \cos\Delta \sin\theta' . \qquad (2)$$

We put this relation into Bragg's equation and solve for d:

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$$d = n\lambda/(2 \cos \Delta \sin \theta') . \quad (3)$$

We see that all orders of reflection would give the same erroneous answer if Δ were neglected, hence one could not detect Δ by a lack of consistency of the d spacings

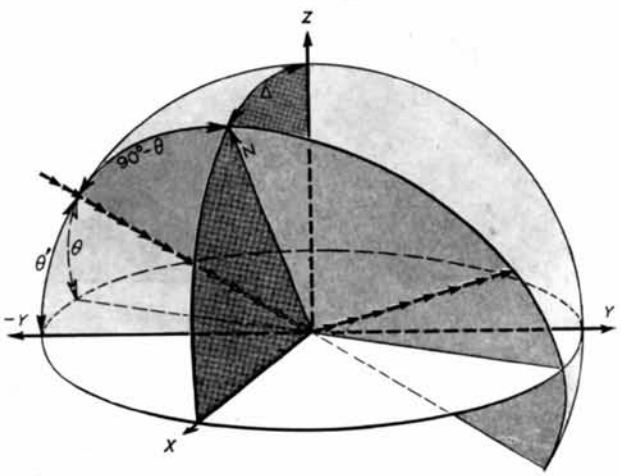

Fig. 2. Apparent θ when the reflecting plane is not parallel to the rotation axis X.

computed from different orders. For d to be in error by no more than one part in 10^m, $\cos \Delta$ must exceed $1-10^{-m}$, or

$$\Delta < (2 \times 10^{-m})^{\frac{1}{2}} \text{ radians} . \quad (4)$$

Hence for accuracy to a part in a million Δ must not exceed 4·8 min. This tells us that the collimator must be perpendicular to the rotation axis within these limits as well as the crystal being oriented within these limits, in fact the sum of the two errors must be within the limits $\pm 4{\cdot}8$ min.

Axial divergence error

If the collimator slit length allows the beam to diverge much outside these limits there may be a slit length correction. Some departure is permissible here since the centroid may still be within limits. If the axial divergence is Δ_0, by averaging the expression $\sin \theta' = \sec \Delta \sin \theta$ (equation (2)) over the limits $\pm \Delta_0$ we find the mean observed angle $\bar{\theta}$ is such that

$$\sin \bar{\theta} = \sin \theta (1 + \Delta_0^2/6 + \dots) . \quad (5)$$

Whence the correct d spacing is

$$d = d'(1 + \Delta_0^2/6) , \quad (6)$$

where d' is the apparent d spacing.

For slits 1 mm. long and 215 mm. apart, $\Delta_0 = 1/215$ whence the correction is 3·6 parts in 10^6. By putting the one mm. length limiting stop on the crystal itself Δ_0 goes to 1/265 and the correction reduces to $2{\cdot}4 \times 10^{-6}\, d'$.

Refraction correction

A correction must be made for refraction. If the diffraction is from a flat surface parallel to the atomic reflecting plane the correction (Compton & Allison, 1935, p. 674) is made by the equation:

$$d = d'(1 + \delta/\sin 2\theta) . \quad (7)$$

The same kind of argument used in deriving equation (7) shows that if the surface is not parallel to the reflecting planes but is rotated from the atomic planes about the measuring axis by amount ε the correction is made by the equation:

$$d = d'(1 + \delta \cos \varepsilon/[\sin (\theta + \varepsilon) \sin (\theta - \varepsilon)]) . \quad (8)$$

If ε is small as compared to θ, (7) gives essentially the same result as (8).

Here δ is unity minus the refractive index of the crystal for the X-ray wavelength used.

$$\delta = ne^2\lambda^2/(2\pi mc^2) , \quad (9)$$

where e is the charge on the electron, m its mass and c is the velocity of light, n being the number of electrons per cm.^{3} (Richtmyer & Kennard, 1947, p. 524). For quick computation we use:

$$\delta = 4{\cdot}48 \times 10^{-6} n_0 \lambda_0^2 , \quad (9')$$

where λ_0 is the wavelength in kXU and n_0 is the number of electrons per cubic kXU.

Lorentz-polarization error

Another source of error to be considered is the displacement of the response curve peak due to the Lorentz and polarization factors. For points near the peak θ_p let us take $x = \theta - \theta_p$ and write the response curve as the Cauchy curve $y = a[1 + (2x/w)^2]^{-1}$ where w is the width at half maximum. This is distorted to $y' = Ly$ where $L = (1 + \cos^2 2\theta)/(2 \sin 2\theta)$ is the Lorentz-polarization factor. Since

$$\frac{dy'}{dx} = L\frac{dy}{dx} + y\frac{dL}{dx}$$

vanishes at θ_p, x is given by

$$\frac{1}{y}\frac{dy}{dx} = -\frac{1}{L}\frac{dL}{dx} .$$

As the peak is displaced less than the half width we may ignore $(2x/w)^2$ as compared to unity. Hence,

$$x = w^2 [\cot 2\theta/4 + \sin 4\theta/[2(1 + \cos^2 2\theta)]] . \quad (10)$$

The absolute value of x is to be added to θ. It is generally very small except at large values of θ.

Dispersion error

It is not known whether the Siegbahn wave lengths are for peak, center of gravity or a compromise. If

the wave lengths refer to peaks there is no dispersion error.

Angle reading errors

We turn now to the question of the accuracy needed in the measurement of θ. Differentiating Bragg's equation we deduce:

$$\Delta\theta = -\Delta d/d \tan\theta\,, \tag{11}$$

whence to measure d to a part in 10^6 at $\theta=75°$ we need to measure θ to $3{\cdot}73\times10^{-6}$ radians$=0{\cdot}77$ sec., while at 85° we would need to measure it to 2·4 sec. Again from Bragg's law the angular line width at half max is

$$\omega = \tan\theta(\Delta\lambda/\lambda)\,, \tag{12}$$

where $\Delta\lambda/\lambda = 300\times10^{-6}$. Whence at 75° $\omega=3{\cdot}8$ min. while at 85° $\omega=13{\cdot}1$ min. At $\theta=75°$, to measure to a part in 10^6 we must divide a line 230 sec. wide at half max and find its center to 0·77 sec. At $\theta=85°$ we must divide a line 700 sec. wide and find its center to 2·4 sec. The line must be centered to about $\frac{1}{3}$% in any case. This means that a line profile will need to be plotted and analyzed and perhaps the results of several determinations averaged.

The instrument

An instrument, Fig. 3 was constructed to operate as in Fig. 1. The collimator is a pair of 50μ slits 215 mm. apart giving an angular beam width at half max of 0·05/215 radians that is 0·8 min. The slits could readily be made finer since the counting rate is adequate (Cu $K\alpha_1$, 13·5 mA., 34 kVP. reflected from (444) of silicon gives 43,000 counts per min.). However, the measured line width above $\theta=40°$ is predominantly due to $\Delta\lambda/\lambda$, not slit size. Hence, narrower slits would not help at the high angles. The crystal is carried by a divided circle gotten from a Hilger Watts microptic clinometer. The circle reads directly to 1 sec. arc.

The counting tubes are Norelco Geiger tubes and two are used so that no weights need be shifted on the instrument frame during a run. The shaft that carries the crystal has its two ends thermally isolated from

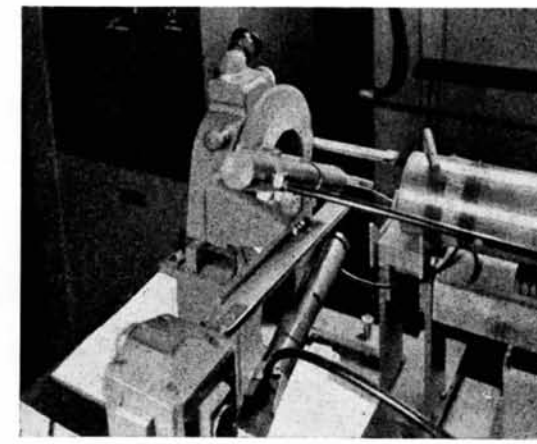

Fig. 3. Photograph of diffractometer.

one another so that the crystal can be maintained at a constant temperature by the passage of water through ducts (see Fig. 4). The crystal end of the shaft and the crystal itself are surrounded by a copper block also temperature maintained by a flow of water and covered with insulation. There is a slot in the block assembly for the passage of X-rays, the slot having a Milar window onto which a thin coat of aluminum has been evaporated.

The crystal must be mounted with the reflecting planes accurately parallel to the axis of the shaft. Since it is not always convenient to grind onto the crystal a facet parallel to the reflecting plane we use an adjustable head that meets the requirements of being compact and unlikely to shift due to temperature changes. This head is shown in Fig. 4. A disk has its upper surface on the center line of the shaft. Its lower face and its chamfered edge are bearing surfaces. The disk can be rotated in its own plane by means of a capstan bar thrust into one of several holes around its cylindrical edge. In this way it can be turned until the crystal cemented to its upper surface has a desired atomic plane parallel to the shaft axis. This condition is brought about by the assistance of an adjusting fixture, Fig. 5. This fixture has a shaft S the same size as the crystal carrier which it now replaces in the

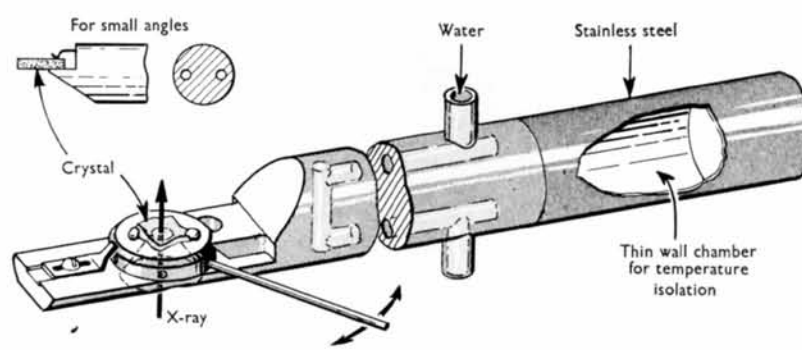

Fig. 4. Crystal carrying shaft.

clinometer while the crystal carrier is placed in a bearing block secured to this fixture shaft. The two shafts are now mutually perpendicular. By rotating the crystal shaft in its block bearing and the fixture shaft (by means of the clinometer) one finds a desired reflection and reads the angle on the clinometer scale. He then turns the crystal shaft approximately 180° and the fixture shaft approximately 180° and finds this reflection again (using the same counting tube) adjusting both the clinometer and the thumb screw T, Fig. 5, for a maximum intensity. If the two clinometer readings do not now differ by exactly 180° the disk is turned by means of the capstan bar to bring the reflection half-way to the point 180° away from the first reading. In this way the two readings are readily made to differ by 180° within a minute of arc, i.e., well within the 4·8 min. required for accuracy to a part in a million. The reflecting planes are now parallel to both shaft axes. The crystal carrying shaft is now inserted in its hole in the clinometer and locked with a thumb screw.

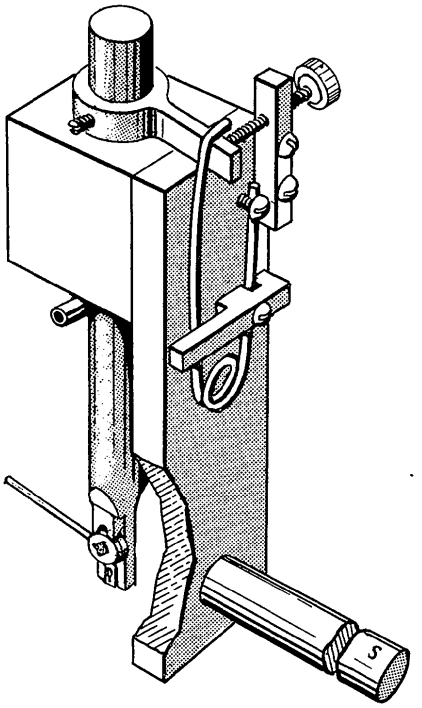

Fig. 5. Crystal adjusting fixture.

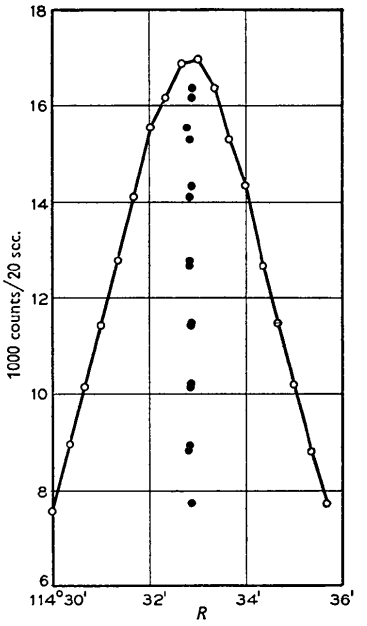

Fig. 6. Analysis of a typical curve—silicon (444) with Cu $K\alpha_1$, $\theta = 79° 18' 45''$.

The Geiger tubes are powered from a Berkeley counting rate meter from which prepared pulses go to a Berkeley EPUT meter which counts the pulses in predetermined time intervals (generally 20 sec.). The EPUT meter is connected to a Berkeley digital recorder which prints the count in each successive time interval.

Fig. 6 is a plot of a reflection from the (444) plane of silicon for which $\theta = 79° 18'$. The Geiger tubes were

Table 1. *Silicon* KB3 (*vacuum floating zone*) $\lambda = 1{\cdot}537395$ kXU

Plane	(444)	(333)	(111)*
θ_1	79° 18′ 45″	47° 28′ 33″	14° 13′ 19·8″
θ_2	79° 18′ 48″	47° 28′ 34″	14° 13′ 21·4″
θ_3	79° 18′ 43″	47° 28′ 35″	14° 13′ 23·3″
θ_4	79° 18′ 39″	47° 28′ 32″	14° 13′ 21·4″
Mean	79° 18′ 43·8″ ± 3·8″	47° 28′ 33·5″ ± 1·3″	14° 13′ 21·5″ ± 1·4″
Line width	6′	1·5′	0·9′
L (corr.)	0·5″	0·0″	0·0″
θ	79° 18′ 44·3″ ± 3·8″	47° 28′ 33·5″ ± 1·3″	14° 13′ 21·5″ ± 1·4″
a_0' (kXU.)	5·419711 at 24·7°	5·419677 at 24·7°	5·419109 at 24·82°
Temp. (corr.)	+0·000004	+0·000004	+0·000002
(a_0') 25°	5·419715	5·419681	5·419111
Refr. (corr.)	+0·000042	+0·000074	+0·000666
Axial diverg.	0·000013	0·000013	0·000013
(a_0) 25°	5·419770	5·419768	5·419790
Std. dev.	0·000019	0·000031	0·000149

* This was done with a special small angle holder shown in the inset, Fig. 4. It is more difficult to adjust the crystal with this holder.

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 2–½ 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 θ/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.

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Some sources of error in precision determination of lattice parameters.

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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: