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Diffraction Patterns of Thin Perfect Crystals and Their Applicability to the Determination of Structure Factors

BY M. RENNINGER

Abteilung 'Interferenzoptik', Betriebseinheit Kristallographie, Philipps-Universität Marburg, Germany (BRD)

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Diffraction patterns containing Pendellösung oscillations produced in different orders of diffraction by thin slices of perfect silicon crystals of different thicknesses have been recorded for both Bragg and Laue cases. The agreement of the curves obtained with those calculated from the dynamical theory is believed to be good enough to allow the derivation of values of the corresponding structure factors. For silicon 422 the value $f_0 = 6{\cdot}81 \pm 0{\cdot}05$ has been found.

I. Introduction

In the early stages of the development of the dynamical theory, Ewald often referred to the oscillations of equal inclination by which diffraction patterns of crystal plates of finite thickness should be 'modulated'. This kind of Pendellösung was not open to observation until recently, although Ewald at that time felt that it would be one of the most satisfactory confirmations of his theory. In those early days, the prohibitive difficulty consisted in finding a way of preparing very thin leaflets of highly perfect crystals. Only when the new semiconductor industry supplied crystals having a perfection previously unknown, crystals which in addition can be prepared without suffering inner damage, did an experimental investigation become possible. Thus, in the special issue of *Acta Crystallographica* in 1968 commemorating P. P. Ewald's 80th birthday three papers simultaneously appeared pursuing that aim, each of them achieving a different partial success: Batterman & Hildebrandt (1968) obtained some records containing a row of side maxima of a Bragg-case diffraction pattern, Kohra & Kikuta (1968) gave a whole Laue-case diffraction pattern, and the author of this paper (Renninger, 1968) obtained whole patterns, in both Laue and Bragg cases, but in an indirect, photographic way only. Further examples of recorded curves were given later by Lefeld-Sosnowska & Malgrange (1968), by Hashizume, Nakayama, Matsushita & Kohra (1970), and finally by Renninger (1969). The endeavours of the latter extended in the mean time to an improved control in preparing thin crystal sheets and furthermore to the quantitative following up and comparing with theory the variation of the curve shapes – of the R_0 as well as of the R_H reflexion – with crystal thickness, for different diffraction orders in the Bragg and Laue cases. The author then tried to find out how far the accuracy reached would be sufficient and useful for precise measurement of structure factors. A summary report on all these attempts will be given below.

II. Theoretical relations

Examples of calculated diffraction patterns as described may already be found in Zachariasen (1945, Fig. 311/12) and in James (1963, Figs. 26 and 31). For the present paper the author worked out programs for calculating systematic rows of patterns for some special cases: the symmetric Laue and Bragg case of the orders 422 and 333 of silicon with Cu $K\alpha$ radiation. The calculations were performed using exact formulae for absorbing crystals, given also by Zachariasen (1945, equations 130/31 and 137/38). These expressions, whose reproduction in detail is dispensed with on account of their complication, are in the form:

$$R_{0,H} = (P_{0,H}/P_0^0)(\Delta\theta, \psi_0, \psi_H, K, \gamma_0, \gamma_H, g, \kappa, d_0, \lambda, \theta_0) \quad (1)$$

where:

P_0^0 power of the primary beam,

P_0, P_H power of the diffracted beams, the undeflected and the deflected one,

$\psi_0 = \psi_0' + i\psi_0''$ forward scattering amplitude,
$\psi_H = \psi_H' + i\psi_H''$ scattering amplitude in direction 2θ,

both defined by the refractive index ν, the structure factor F and the absorption coefficient μ as follows:

$$\psi_0' = -2(1-\nu) \quad (2)$$

$$\psi_0'' = -\frac{\lambda}{2\pi} \cdot \mu\,, \quad (3)$$

$$\psi_H' = \frac{F_H'}{\sum(Z_j + \Delta f_{0j})}\,\psi_0'\,, \quad (4)$$

$$\psi_H'' = \frac{\sum \Delta f_j'' \cdot \exp(2\pi i H r_j - M_j)}{\sum \Delta f_{0j}''} \cdot \psi_0''\,. \quad (5)$$

For convenience the following connecting quantities are introduced which contain mainly the effect of accounting for finite absorption:

$$g=\frac{1-b}{2\sqrt{|b|}}\cdot\frac{1}{K}\cdot\frac{\psi_0''}{|\psi_H'|}, \tag{6}$$

$$\kappa=\frac{|\psi_H''|}{|\psi_H'|}; \tag{7}$$

γ_0 and γ_H are the direction cosines of primary and deflected beam, γ_0 being cos θ in the symmetric Laue, sin θ in the symmetric Bragg case. $b=\gamma_0/\gamma_H$, the degree of asymmetry of the reflexion (>0 in Laue case, <0 in Bragg case), K – Polarization factor, equal to one and $|\cos 2\theta|$ for the two directions of polarization. For special cases (symmetrical cases and 2θ near $\pi/2$) the values of $|b|$ and K are 1.

In order to reach a certain typical and general character for the results, norm scales for the angular variable and for the crystal thickness are introduced instead of the corresponding absolute scales:

(1) A norm thickness d_n connected with the absolute thickness d_0 by the relation:

$$d_n=\frac{K\,.\,|\psi_H'|}{\lambda\sqrt{|\gamma_0\gamma_H|}}\,.\,d_0\,, \tag{8}$$

which for the present special cases becomes

$$d_n=\frac{|\psi_H'|}{\lambda\,.\,\gamma_0}\,.\,d_0\,. \tag{8'}$$

d_n is, up to a factor π, identical with the symbol A introduced by Zachariasen.

(2) A normalized angular variable y, related to the absolute one, $\Delta\theta$, by:

$$y=\frac{1}{K}\cdot\frac{\sin 2\theta_B}{|\psi_H'|}\,.\,\Delta\theta\,. \tag{9}$$

$\Delta\theta$ is defined so as always to run in the same sense as θ and to have its zero value at the centre of the R_H diffraction pattern (in the Bragg case the one for zero absorption). y too is identical with the corresponding variable y of Zachariasen, apart from a factor $-b/|b|$ from whose omission the equality of sign of y and $\Delta\theta$ follows, in the Bragg as well as in the Laue case.

The numerical values of the quantities used for the calculation were taken from literature and are collected in Table 1.

With the values of Table 1, R_H and R_0 patterns for Laue and Bragg cases have been computed and automatically plotted as a function of y and of $\Delta\theta$ for 16 values of d_n between 0·5 and 2·0.

The theoretical curves presuppose a strictly monochromatic and plane primary wave which is given only approximately by the double-diffractometric device used for recording. The angular width of the beam reflected there by the first, the 'monochromator' crystal is 1·1″ for 422 and 0·8″ for 333. To make allowance for this a second row of calculations was performed parallel to the one described above, $R_{0,H}^{M}(\Delta\theta)$, where the intrinsic diffraction pattern is convoluted with the angular distribution of the primary beam. Exact convolution was replaced for simplicity by an approximate one, where for each abscissa $\Delta\theta$ the intrinsic $R_{0,H}$ values were replaced by their mean values within the angular ranges given. As expected, this procedure causes a smoothing of the extreme values, but, with the exception of the first pair of side maxima, no angular displacement of them. This may at first seem surprising, but it should be expected, as long as the averaging range is smaller than the distance between neighbouring maxima.

Table 1. *List of values used*

	422 Laue case	422 Bragg case	333 Laue case	333 Bragg case
θ_B	44·1°		47·5°	
$d_H=\lambda/2\sin\theta$	1·109		1·045	
$\gamma_0=\lvert\gamma_H\rvert$	0·718	0·693	0·676	0·737
$\mu(\mathrm{cm}^{-1})$	146			
$\delta=1-\nu$	$7{\cdot}5\,.\,10^{-6}$			
f_0	6·44			
$\Delta f'$	0·22			
$\Delta f''$	0·33			
ψ_0'	−150			
ψ_0''	−3·53			
$\lvert\psi_H'\rvert$	6·85		4·55	
$\lvert\psi_H''\rvert$	3·22		2·28	
$\times 10^7$				
g	−0·0515		−0·0776	
κ	0·047		0·051	
$\exp(-M)$	0·914		0·909	

A selection of the calculated patterns is given in Fig. 1 for norm thickness 0·5, 0·75, 1·0, 1·4 and 2·0, 422 only, Laue cases on the left, Bragg cases on the right.

III. Experimental data

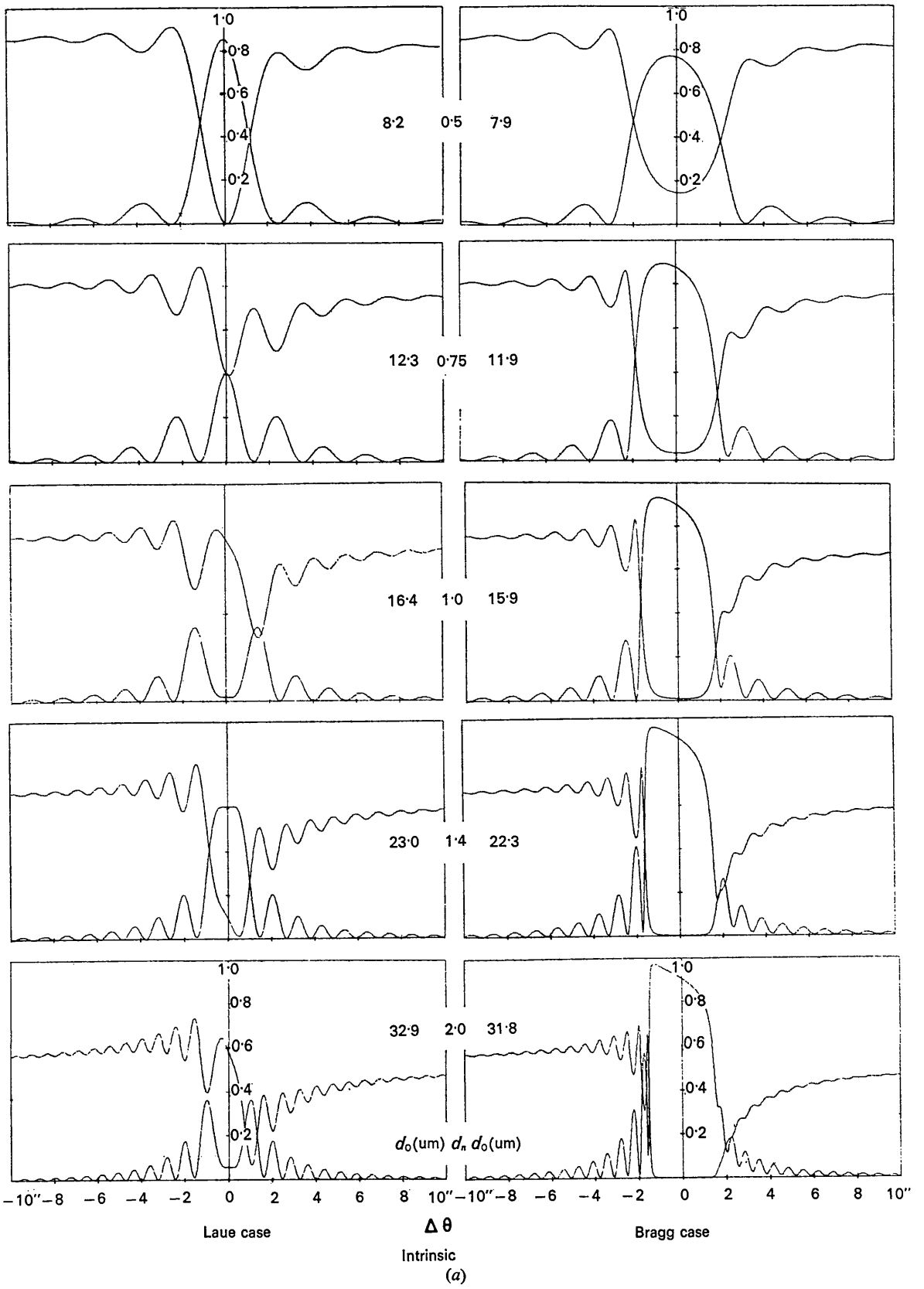
1. *Preparation of crystal sheets*

The range of norm thickness which is mainly of interest, between 0·5 and 2·0, corresponds to an absolute thickness between 8 and 40μm. To prepare crystal sheets of that order of thickness two ways are available and have both been tried: (*a*) Etching out a circular area from a thicker wafer, (*b*) Grinding down whole wafers followed by a semichemical polish on cloth with colloidal SiO_2 suspension (A'Aerosil' polish).* The advantage of method (*a*) lies in the easy manipulation of the sheets, resulting from the fact that the thinned part is supported by the surrounding ring of thicker material continuing its lattice and thus avoiding any stress. The advantage of (*b*) is the avoidance of strong thickness gradients.

2. *Recording technique*

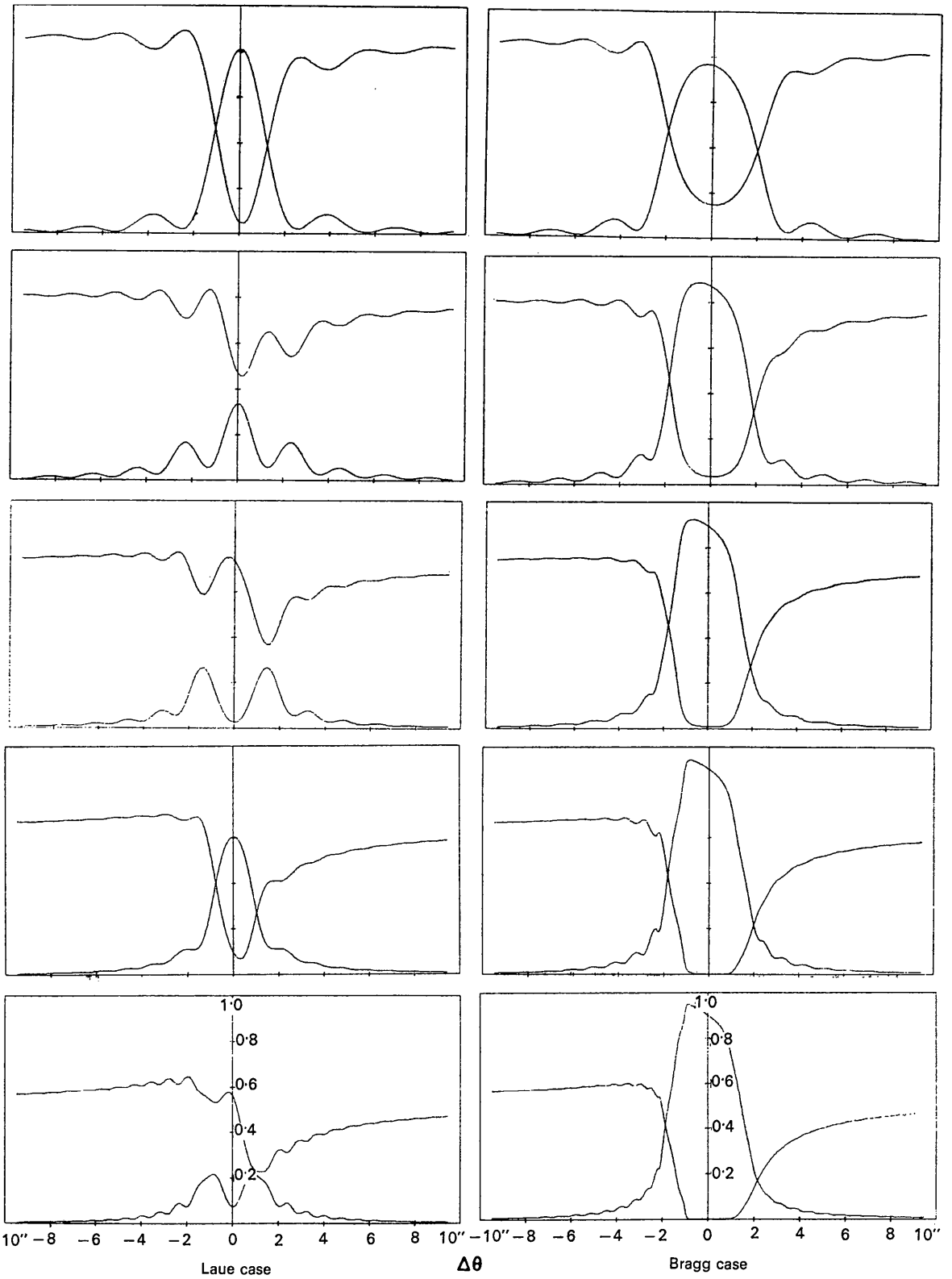
The double-diffractometric device for taking the records is nearly the same as that described repeatedly earlier (Renninger, 1963, 1964, 1965) and is shown in

* I am obliged to Dr K. Mayer, Siemens, München for preparing sheets of the first kind and to Dr Deckert, Wacker Chemitronic, Burghausen for preparing sheets of the second kind.



(*a*)

Fig. 1. (*a*) Theoretical diffraction patterns (422). (*a*) Intrinsic.



(*b*)

Fig. 1. (*cont.*) (*b*) Convoluted with the angular distribution of the primary beam.

Fig. 2. A first crystal prepared for strongly asymmetric V reflexion ($\beta=-0{\cdot}92$, $b=-24$), of an order the same as that of the sample (or at least with equal $\sum h^2$), offers to the second crystal a primary beam of large cross section but small angular divergence. A diaphragm B measurably movable horizontally and vertically allows an exact choice of the location of the reflecting area on the sample. It may be removed and readjusted reproducibly. The counter, pivotable around the second axis, may take up either the power of the deflected beam, P_H, or that of the undeflected one, P_0, and also, with the sample removed, that of the primary beam coming from the first crystal, P_0^0. The ratio of these latter two powers (P_0 with the sample at an angular position somewhat away from a direction of diffraction) is a measure of the weakening by absorption, and hence of the thickness d_0 at the reflexion position. By measuring the thickness in that way over the whole area of the sheet, reached by moving the diaphragm B in both directions, a thickness topograph of the sample is obtained which then allows the choice of a reflecting place of desired thickness. This choice, is additionally determined by the requirement that no lattice defects are present nearby. This may be tested by X-ray topographs doubly exposed, with and without the diaphragm B. Fig. 3 shows such a topograph (422 transmission topograph, R_0 and R_H together). As for the cross section of the diaphragm, a compromise had to be attempted between the requirement of a high intensity (to give a reasonable recording time) and the necessity for sufficient constancy of thickness and orientation within the reflecting area. A value between 0·1 and 0·15 mm² was chosen as a rule. Additionally the shape was chosen as rectangular, the short side orientated nearer the direction of the thickness gradient.

The first trial records of diffraction curves were taken by separate synchronized driving of crystal and recorder. However this method revealed irregular variations in the speed coordination, and therefore up to 5% variation in the abscissa scale of the records, preventing exact angular evaluation. This matter gave rise to the search for an immediate measure of the crystal's angular position to be employed for abscissa input to an x–y recorder. For such a measurement an

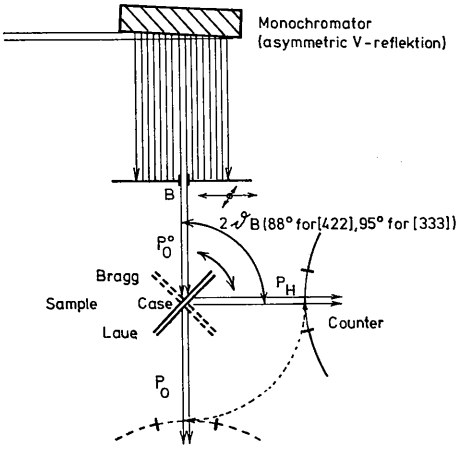


Fig. 2. Scheme of the experimental device.

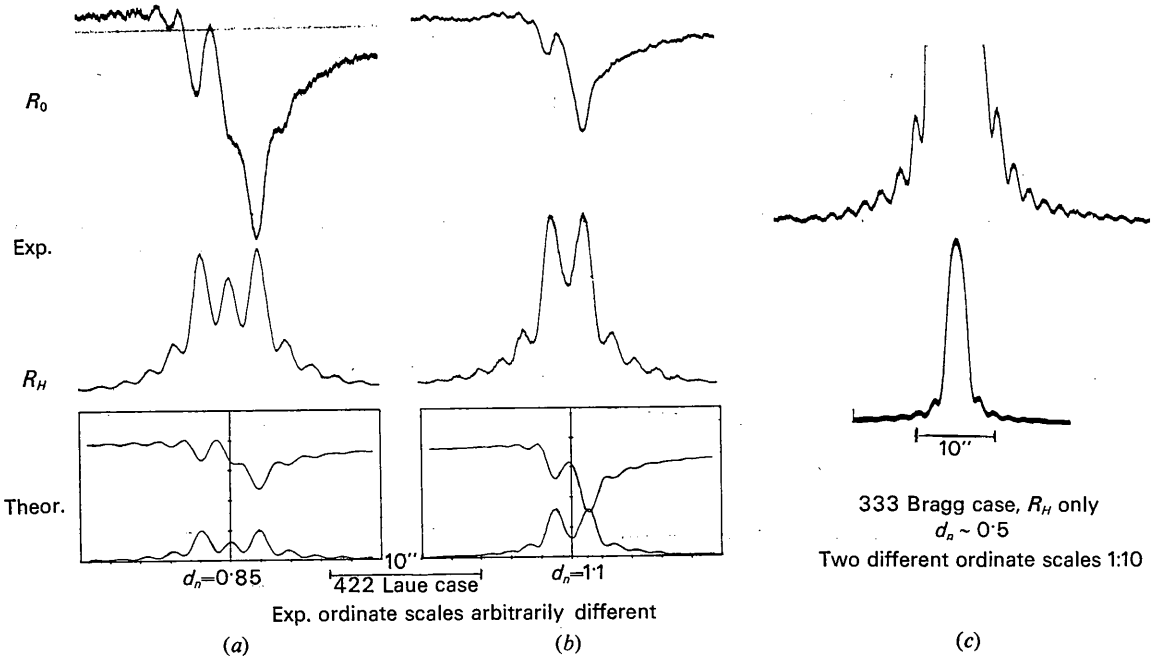
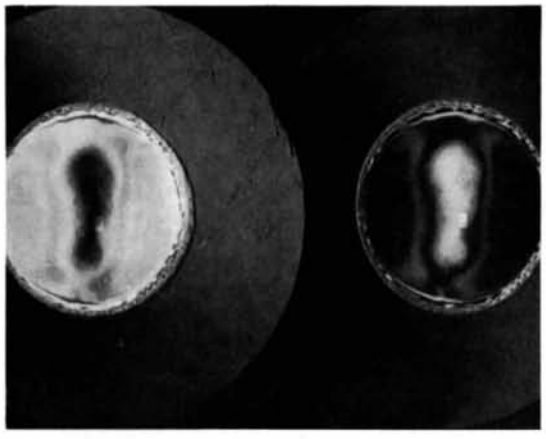


Fig. 4. Examples of measured patterns together with the theoretical ones. (*a*) 422 Laue case, $d_n=0{\cdot}85$. (*b*) 422 Laue case, $d_n=1{\cdot}1$. (*c*) 333 Bragg case, $d_n=0{\cdot}5$, R_H only, on two ordinate scales, different by a factor 10 [as for the theoretical curve; see Fig. 1(*b*)].



422 transmission

Fig. 3. Example of a topograph for fixing the point of reflexion.

[*To face p.* 46

accuracy of one hundredth of a second of arc is necessary. This was achieved by an autocollimation telescope governed electronically by the use of an oscillating slit (Photoelektrischer Messtubus, Leitz, Wetzlar). The collimating mirror for its use is fixed on the specimen holder.

In terms described above, the time needed for one record (crystal turned by 30 to 60″) was 15 to 30 min, which is 30 s for one second of arc.

IV. Results

1. *General*

Fig. 4 gives some characteristic examples of diffraction-pattern records, each in comparison with corresponding theoretical curves computed as described in § II.

2. *Method of evaluation for determination of structure factor*

The fascinating possibility of using Pendellösung diffraction patterns for measurement of structure factors results from the fact that no further experimental data beyond the angular ones contained in the curves themselves are needed for the evaluation. For example no exact measurement of the *absolute* sheet *thickness* is necessary, for this latter is rather given by the angular distance of the *outer maxima* of the curve. The *norm thickness* d_n, on the other hand, manifests itself in the distance of the first maximum and the general curve shape. The two values combined fix the structure factor.

The procedure of evaluation was chosen as follows: From the series of theoretical diffraction curves computed on the basis of literature data diagrams are derived in which families of curves give not only the angular distance of all side maxima as a function of the sheet thickness, but also the dependence of y_{Mi} on d_n as well as that of $\Delta\theta_{Mi}$ on d_0. Fig. 5 shows such a diagram for the 422 Laue case. In the y–d_n scale this diagram may be considered as valid for any other diffraction order or crystal. For in terms of this scale the diagram is not noticeably different from one computed by the use of the simple formula for non-absorbing crystals:

$$R_H = \frac{\sin^2(\pi d\sqrt{1+y^2})}{1+y^2}$$

(Zachariasen 1946, p. 131).

The influence of the absorption on the angular distance of the maxima (not of course on their height) is imperceptibly small.

With the aid of the $\Delta\theta_{Mi}$–d_0 scale of the diagram, valid for the particular diffraction order chosen, the absolute thickness d_0 from a given experimental diffraction curve is now obtained by measuring the angular distances of all Pendellösung maxima and entering them on a separate scale which is then shifted on the diagram in a horizontal direction until it optimally fits on the ordinate values of the family of curves. Then the abscissa location of that auxiliary scale gives the value of d_0.

In order to obtain d_n, two conditional equations are available. Firstly there is the universal connexion between y_{Mi} and d_n for the first (eventually, but much less exactly, also the second) side maxima, rendered by the lowest curve of Fig. 5. The other conditional equation is contained in the connexion between the norm variables, y and d_n, and the absolute ones, $\Delta\theta$ and d_0 [combination of equations (8) and (9)]. For a given, measured pair of values of $\Delta\theta_{M_1}$ and d_0 we have the reciprocity relation:

$$d_n = \frac{d_0 \cdot \Delta\theta_{Mi}}{d_H} \cdot \frac{1}{y_{Mi}} = \alpha \cdot \frac{1}{y_{Mi}} \qquad (10)$$

(d_H–interplanar distance).

The d_n value resulting from the measured diffraction pattern is thus given by the abscissa of the intersection between the function $y_{Mi}(d_n)$ and the equilateral hyperbola $y_{Mi} = \alpha/d_n$. This intersection has to be determined graphically since $y_{M1}(d_n)$ is not known explicitly. Because the intersection is very flat a vertical shearing of the coordinate system to an oblique one is convenient. In such a system Fig. 6 contains the $y_{M1}(d_n)$ curve of Fig. 5 and sections of α/d_n hyperbolas for four values of the parameter α (0·6, 0·8, 1·0, and 1·2). The rectangularly framed area is given magnified in Fig. 6(*b*), once more with a series of hyperbola sections in narrower steps of α. From this figure, graphically again, the direct connexion between α and d_n is derived and reproduced in Fig. 7, which then allows d_n to be obtained from the experimental data alone. The values of d_n and d_0 immediately define the structure factor:

$$|\psi'_H| = \lambda \cdot \cos\theta \cdot \frac{d_n}{d_0} \qquad (11)$$

$$|F'^{290°}_H| = \frac{\pi a^3}{e^2/mc^2 \cdot \lambda^2} \cdot |\psi'_H| = \frac{\pi a^3 \cos\theta}{e^2/mc^2 \cdot \lambda} \cdot \frac{d_n}{d_0} \cdot \qquad (12)$$

The real part of the structure amplitude for the single resting, silicon atom then becomes

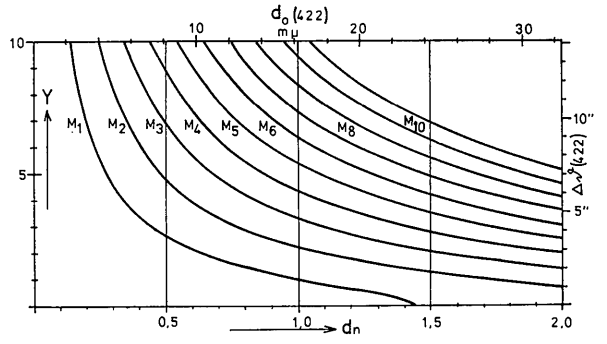


Fig. 5. Angular distance of the Pendellösung maxima M_1–M_{10} as a function of thickness.

$$f_0 = \frac{\exp M}{|S|} \cdot F'^{290°} - \Delta f' \qquad (13)$$

$|S| = 8$ (even indices).

3. *Synopsis and discussion of the results*

In Table 2 the results of all records suitable for quatitative evaluation are compiled (422 Laue case only). They include measurements on crystal sheets of a thickness range between 12 and 20 μm (d_n between 0·8 and 1·2), six groups of measurements, each containing a number ν (specified in the second row) of records obtained under identical conditions.

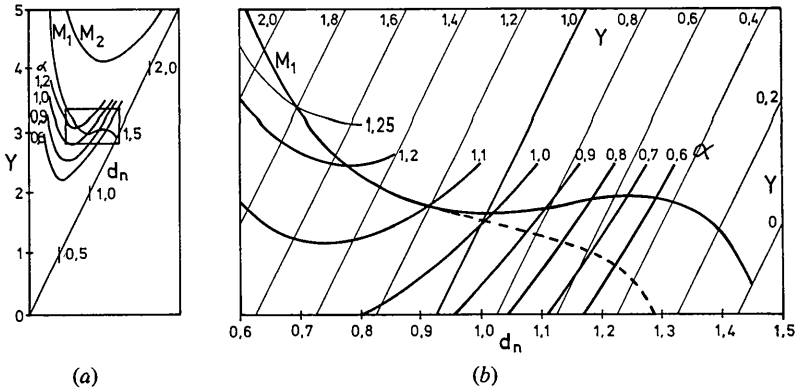
The limits of error given in row 11 are the standard deviations of the mean values of each group of measurements derived from the statistical scatter of the single values. In Fig. 8 the resulting structure factors of each group are represented once more, together with their standard deviations. It seems striking that those statistical limits of the single groups are smaller than the mutual scatter between them. This statement seems to point to an unknown systematic error depending on the choice of the respective reflexion area. Possibly small lattice distortions or a small thickness gradient within it may be responsible.

The weighted mean for $f_0^{290°}$ rendered in row 11 remains in the range of earlier literature data, but deviates significantly from the value which has seemed the best until now, measured by Kikuta, Matsushita & Kohra (1970) and later on, improved, by Nakayama, Kikuta & Kohra (1971) from the angular width of the Bragg-case diffraction pattern of thick crystals.

In summary it may be said that the method for determination of structure factors described here is not yet quite comparable in precision with the one reached by Kohra and collaborators. But it may doubtless be essentially improved by further refinement of the angular measurements and of the preparation of thin crystal sheets. The objection that the method is relatively complicated and therefore scarcely practicable in general may be countered by remarking that the main difficulty in applying it consists of the necessity of having a monochromator crystal reflecting asymmetrically a diffraction order identical with that of the sample. This requirement may however be overcome by application of an universally usable (n, ±

Table 2. *Compilation of results*

1	Group of measurements (Number)	I	II	III	IV	V	VI
2	Number ν of single records in each group	15	9	3	9	4	12
3	d_0(μm) (from $\Delta\theta_{M_{1-6}}$)	12·90	13·60	14·30	14·92	18·02	18·51
4	$\Delta\theta_{M_1}$ (seconds of arc)	$2{\cdot}08_5$	$1{\cdot}96_5$	1·75	1·66	1·05	0·982
5	α	1·177	1·169	1·093	1·085	0·828	0·795
6	d_n (from Fig. 7)	0·811	0·823	0·921	0·930	1·120	1·136
7	d_0/d_n	15·91	16·52	15·53	16·04	16·09	16·29
8	$\lvert\psi'_H\rvert$ ($\times 10^6$)	69·6	67·1	71·3	69·1	68·9	68·0
9	$F'^{290°}_{CuK} = \frac{\pi a^3}{e^2/mc^2 \cdot \lambda^2} \cdot \lvert\psi'_H\rvert$	52·2	50·3	53·5	51·8	51·6	51·0
10	f_0 Single values	6·89 ±0·06	6·64 ±0·07	7·08 ±$0{\cdot}04_5$	6·84 ±0·05	6·82 ±0·03	6·72 ±$0{\cdot}02_5$
11	f_0 Weighted mean	6·81 ±0·05 (0·8 %)					
12	f_0 Weighted mean of earlier measurements (Miyake, 1969)	6·82 ±0·04 (0·6 %)					
13	f_0 Kikuta, Matsushita & Kohra (1970) and Nakayama, Kikuta & Kohra (1971)	6·708 ±0·006 (0·1 %)					



(*a*) (*b*)

Fig. 6. Curve for M_1 and M_2 of Fig. 5 in a sheared coordinate system together with sections of hyperbolas, α/y_M . (*b*) repeats the area rectangularly framed in (*a*) on a larger scale. The dotted branch of the M_1 curve allows for the angular distribution of theprimary beam [see Fig. 1(*b*)].

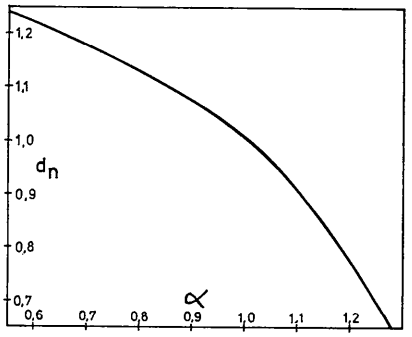


Fig. 7. Relation between d_n and α derived from Fig. 6 (dotted branch).

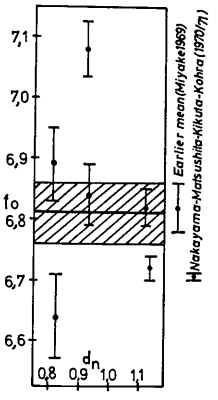


Fig. 8. Single and mean results for f_0.

m) double monochromator (Renninger, 1938, 1955; Kohra, Hashizume & Yoshimura 1970). That means, it is true, a great loss of intensity which however may be compensated by other provisions (more X-ray power, longer measuring times, greater reflecting areas). Then the method should become comparable to other precision methods.

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References

BATTERMAN, B. W. & HILDEBRANDT, G. (1968). *Acta Cryst.* A**24**, 150–157.
HASHIZUME, H., NAKAYAMA, K., MATSUSHITA, T. & KOHRA, K. (1970). *J. Phys. Soc. Japan*, **29**, 806.
JAMES, R. W. (1963). *Solid State Phys.* **16** (C), 53–220.
KIKUTA, S., MATSUSHITA, T., & KOHRA, K. (1970). *Phys. Lett.* **33**A, 151–152.
KOHRA, K., HASHIZUME, H. & YOSHIMURA, J. (1970). *Jap. J. Appl. Phys.* **9**, 1029–1038.
KOHRA, K. & KIKUTA, S. (1968). *Acta Cryst.* A**24**, 200–205.
LEFELDS-SOSNOWSKA, M. & MALGRANGE, C. (1968). *Phys. Stat. Sol.* **30**, K23–25.
MIYAKE, S. (1969). *Acta Cryst.* A**25**, 257–264.
NAKAYAMA, K., KIKUTA, S. & KOHRA, K. (1971). *Phys. Lett.* **37**A, 29–30.
RENNINGER, M. (1938). *Z. Kristallogr.* **99**, 181–187.
RENNINGER, M. (1955). *Acta Cryst.* **8**, 597–606.
RENNINGER, M. (1963). *Crystallography and Crystal Perfection*, Edited by G. N. RAMACHANDRAN, pp. 145–152. New York: Academic Press.
RENNINGER, M. (1964). *Z. Naturforsch.* **19***a*, 783–787.
RENNINGER, M. (1965). *Z. angew. Phys.* **19**, 20–33.
RENNINGER, M. (1968). *Acta Cryst.* A**24**, 143–149.
RENNINGER, M. (1969). *Acta Cryst.* A**25**, S 214.
ZACHARIASEN, W. H. (1945), *Theory of X-Ray Diffraction in Crystals.* New York: John Wiley.