Table 1 (*cont.*)

Equator position, inclination of incident beam
Beam divergence (axial, equatorial); specimen height (interference-cone overlapping)
Angle measurements; counter movement; pulse registration
Beam absorption or transparency of the specimen
Temperature of the specimen
Refraction in the specimen

(c) *Errors of measuring procedure* (approximations in methods of measurement and evaluation; errors of calibration; standard comparison)

Incorrect scale (measurement, evaluation)
Angle functions in extrapolation methods
Correction for refraction (dependent on condition of crystal)
Wavelength uncertainty; asymmetry of emission lines
Absolute determination of the *X* unit

('exterior error') or whether it is obtained without regard to the squares of the deviation as 'interior error'

$$\tilde{m} = \{\Sigma 1/p_i\}^{\frac{1}{2}} = \pm 0{\cdot}000\ 02\ \text{Å}; \quad 1/\tilde{m}^2 = \Sigma 1/m_i^2 .$$

m is the uncertainty of measurement of the final result of each institute calculated on the assumption that m contains only random errors. $\tilde{m}$ turns out smaller than $\tilde{m}_p$, and so, in accordance with error theory, it shows the existence of some systematic errors. To estimate their amount, Δa, in the IUCr total result the ordinary root-mean-square error

$$\Delta a \approx \tilde{m} = \{\Sigma(\bar{a}_i - \bar{\bar{a}})^2/(n-1)\}^{\frac{1}{2}}$$

can be applied. About two-thirds of all the final results $\bar{a}$ reported by the institutes lie within the limits $\Delta a = \pm 0{\cdot}0002$ Å. This estimate might represent a reasonable criterion for the residual portions of the systematic errors. In it the differences between the institute values are formally treated as random deviations. This is a valid procedure in this case, because the number n of the participating institutes is not too small, and further because their final results are distributed rather regularly around the total result $\bar{\bar{a}}$ of the IUCr. Compared with this residual portion Δa of the mean systematic errors, the random errors of the total result, $\tilde{m}_p = 0{\cdot}000\ 04$ Å, are not important.

The final result $\bar{\bar{a}} = 5{\cdot}430\ 64$ Å is obtained from an arithmetic mean with weighting factors p; the results are different depending on whether weighting factors are introduced,

$$\bar{\bar{a}}_p = \Sigma p_i . \bar{a}_i / \Sigma p_i = 5{\cdot}430\ 64\ \text{Å},$$

or not

$$\bar{\bar{a}}_0 = \Sigma \bar{a}_i / n = 5{\cdot}430\ 54\ \text{Å}.$$

Thus as total result for the lattice parameter of the silicon, on the conditions agreed, there results

$$a_{\text{Si}} = (5{\cdot}430\ 64\{1 \pm 3{\cdot}7 \times 10^{-5}\} \pm 0{\cdot}000\ 04)\ \text{Å},$$

where the brackets contain the estimated residual portion of the mean systematic error, or briefly

$$a_{\text{Si}} = (5{\cdot}430\ 6_4 \pm 0{\cdot}0002)\ \text{Å}.$$

Attention may once more be drawn to the—in some respects dubious—assumption underlying this error discussion, namely that the reported uncertainties m contain essentially only the random errors of the institutes. Otherwise, the discussion of error becomes still more difficult or even impossible. This shows the necessity of a precise and detailed specification of the experimental uncertainties of each institute and the advantage of knowing which of the systematic errors were treated in detail in the error elimination. Lastly, an attempt at classifying the many possibilities of errors arising is given in Table 1.

Perhaps the available IUCr comparison measurements cannot yet, strictly, be regarded as ultimate; but in any case they are a very valuable basis for further cooperation.

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The ratio method for absolute measurements of lattice parameters with cylindrical cameras.

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Introduction

The principle of the ratio method for cubic lattices consists in using two diffraction lines for determining the individual values of the lattice parameter. For two-parameter lattices three or four diffraction lines are to be taken. In this way a knowledge of the distance specimen-film or of the camera radius is not needed.

For cubic lattices the method was described in various forms by several authors (Wever & Möller, 1933; Rovinskij, 1940; Černohorský, 1952; Becherer, Brümmer & Ifland, 1955; Rovinskij & Kostiukova, 1958). For two-parameter lattices the method was described also (Matějka, 1956). However, only a flat camera or a cone camera (Kochanovská, 1943) was used. The use of cylindrical cameras has been described recently (Černohorský, 1959*a*).

The present paper shows how to determine *a priori*

the accuracy as a function of the choice of the diffraction lines. In addition, the results of measurements are presented as to illustrate the possibilities of the ratio method used with cylindrical cameras.

It seems indicated to give here briefly the principle of the ratio method applied with cylindrical cameras.

Cubic lattices

The parameter a can be determined from the equation

$$\frac{l_i}{l_j} = \frac{\frac{1}{2}\pi - \arcsin\left[(\lambda_i/2a)(h_i^2+k_i^2+l_i^2)^{\frac{1}{2}}\right]}{\frac{1}{2}\pi - \arcsin\left[(\lambda_j/2a)(h_j^2+k_j^2+l_j^2)^{\frac{1}{2}}\right]},$$

where l is the length corresponding to the angle $2\pi - 4\theta$. A pair of diffraction lines is thence needed. We compute the right side of the equation for equidistant arguments a. Thus we obtain a table where the lattice parameter corresponding to the ratio of the measured values l_i, l_j is found.

Tetragonal lattices

For tetragonal lattices we compute the ratio

$$\frac{\frac{1}{2}\pi - \arcsin\left[(\lambda_i/2a)(h_i^2+k_i^2+l_i^2u^2)^{\frac{1}{2}}\right]}{\frac{1}{2}\pi - \arcsin\left[(\lambda_j/2a)(h_j^2+k_j^2+l_j^2u^2)^{\frac{1}{2}}\right]}$$

for equidistant values of a and u ($u=a/c$). In the coordinate system with axes a, u a line corresponds to the ratio belonging to a pair of diffraction lines. This line has been called the isomorionic line, i.e. a line where the ratios have the same values, as explained in detail and illustrated in the paper cited (Černohorský, 1959*a*, p. 146). Each pair of diffraction lines gives us an isomorionic line. The point of intersection of two isomorionic lines determines the lattice parameters.

Hexagonal lattices

The application to the hexagonal lattices is obvious.

Accuracy functions

For different cases it is possible to establish an accuracy function Z defined by the relation

$$\Delta P/P = Z(\Delta a/a)\,. \tag{1}$$

The values of this accuracy function, the so-called accuracy factors, state how many times the relative accuracy of the evaluated lattice parameter a is greater than the relative accuracy of the ratio P of the directly measured values (Černohorský, 1959*b*). If these values are represented by the intervals l (i.e. $P_{ij}=l_i/l_j$), then we have an absolute method called the ratio method (Černohorský, 1952).

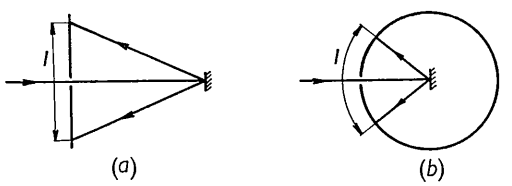

Fig. 1. Geometrical arrangement.

The accuracy function of the ratio method for cubic lattices is given for the flat camera (Fig. 1(*a*)) by formula (2) and for the cylindrical camera (Fig. 1(*b*)) by formula (3):

$$Z_F = w_1 - w_2,\quad w = 4\tan\theta\ \mathrm{cosec}\ 4\theta; \tag{2}$$

$$Z_C = z_1 - z_2,\quad z = (\tfrac{1}{2}\pi - \theta)^{-1}\tan\theta\,. \tag{3}$$

The accuracy factors in the entire region of Bragg angles above 60° are greater in the case of the cylindrical camera. The difference of accuracy factors is, however, only of slight quantitative significance, so that from the viewpoint of accuracy factors both methods are practically equally convenient. However, with respect to the perpendicular incidence of the diffracted beams to the film, the cylindrical camera is much more convenient than the flat camera.

For two-parameter lattices the relation

$$\Delta P/P = Z_a(\Delta a/a) + Z_u(\Delta u/u),\quad u = a/c \tag{4}$$

can be derived, where the accuracy functions take the forms

$$Z_a = z_1 - z_2,\quad z = (\tfrac{1}{2}\pi - \theta)^{-1}\tan\theta\,, \tag{5}$$

$$Z_u = -(z_1/M_1) + (z_2/M_2)\,, \tag{6}$$

where

$$M = 1 + m/(l^2u^2),\quad m = \begin{cases} h^2+k^2 & \text{(tetragonal)} \\ \frac{4}{3}(h^2+hk+k^2) & \text{(hexagonal)} \end{cases} \tag{7}$$

Thus Z_a is identical with the accuracy function (3) for cubic lattices whereas Z_u depends not only on the Bragg angle but also on the Miller indices and on the ratio of lattice parameters. As both the function z and the function M can be tabulated the determination of the accuracy factors Z_a and Z_u in actual cases is very rapid.

Isomorionic belts for two-parameter lattices

The idea of making use of the accuracy functions resides in the possibility of *a priori* estimation of the characteristics of the diffraction lines convenient for the ratio method. With respect to the limited accuracy of the measured values it is advisable not to work with isomorionic lines, but with isomorionic belts (Fig. 2). The

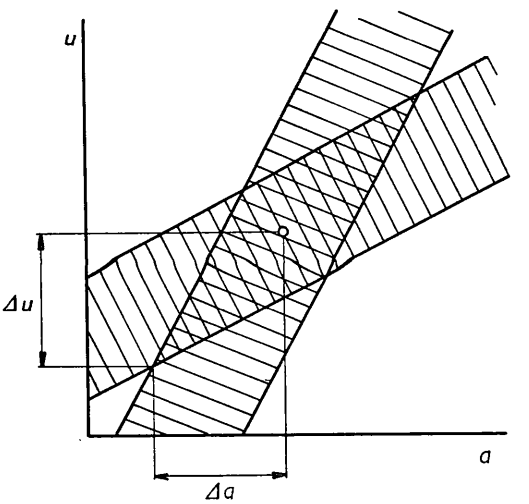

Fig. 2. Isomorionic belts. Each belt is given by the ratio $P_{ij}=(l_i \pm \Delta l_i)/(l_j \pm \Delta l_j)$ and by characteristics of the diffraction lines in question (θ, hkl).

Table 1. *Lattice parameters of ruthenium* ($t = 21._8$ °C.)

	Quartet of lines		Z_a	Z_u	Z_a/Z_u	a	a/c
1	Ni α_2 114	Cu α_2 300	4·3	29·1	0·147	2·7057 Å	0·63205
	Ni β 213	Cu α_1 105	130·8	29·6	4·42		
2	Ni α_1 114	Ni α_2 211	28·2	23·8	1·18	2·7058	0·63206
	Cu α_2 300	Cu α_2 204	21·7	−11·7	−1·85		
3	Ni α_2 114	Cu α_1 300	12·0	29·1	0·41	2·7056	0·63201
	Ni β 213	Ni α_1 114	102·4	15·2	6·74		
4	Ni α_1 114	Ni α_1 211	28·8	23·9	1·21	2·7058	0·63201
	Cu α_1 300	Cu α_2 204	14·0	−11·7	−1·20		
5	Cu α_2 300	Ni α_1 114	3·5	−24·3	−0·14	2·7059	0·63205
	Cu α_2 300	Ni α_1 211	32·3	−0·4	−80·8		
6	Ni α_2 114	Ni α_2 211	36·0	28·6	1·26	2·7058	0·63206
	Cu α_1 300	Cu α_1 204	16·3	−10·4	−1·57		
7	Ni α_1 114	Cu α_1 300	4·2	24·3	0·17	2·7057	0·63203
	Cu α_1 300	Ni α_2 211	24·0	−0·5	−48·0		
8	Ni α_2 114	Ni α_1 211	36·6	28·7	1·28	2·7059	0·63205
	Cu α_2 300	Cu α_1 204	24·0	−10·4	−2·31		
					Mean value	2·7058 Å ±0·0001 Å	0·63204 ±0·00002

common part of both belts answers the ratio of values measured with the respective accuracy. In order that the errors of the measured lattice parameters may be small it is necessary for the isomorionic belts to be narrow, i.e. at least one of the values Z_a, Z_u must be great. Furthermore, it is convenient for the isomorionic belts not to intersect at a small angle but, if possible, to be perpendicular one to the other. It is therefore desirable to find such combinations of diffraction lines that give a high value Z_a or Z_u and very different slopes $aZ_a/(uZ_u)$ for the two isomorionic belts.

Experimental

The results of this analysis have been applied to ruthenium. It appeared to be convenient to use nickel and copper radiation. The camera diameter was 114·6 mm., the powder specimen of ruthenium (at least 99·5%) was flat. The pattern measurement was done by means of an Abbe comparator of Zeiss make. Eight quartets of diffraction lines were chosen in such a way that each quartet brought into being a pair of isomorionic belts approximately perpendicular to each other. The results are given in Table 1.

The resulting accuracy is satisfactory if we take into consideration the experimental simplicity of the method and the fact that the directly measured values were not corrected in any way and no extrapolation procedures were used. Systematic errors, undoubtedly present, are eliminated simply through the fact that we work with the ratio of measured values. Of course, they are eliminated only as far as they are proportional to the supplement of the Bragg angle. The non-linear part of systematic errors can manifest itself only if the precision of the measurement is high enough. As it is desirable to follow the systematic errors as a function of the Bragg angle, a useful feature of the ratio method carried out with the cylindrical camera resides in the fact that the diffraction lines with Bragg angles as small as 60° may be used.

To determine the magnitude of the systematic errors, a substance with cubic lattice may be used. If we combine a given diffraction line successively with all the others we can conveniently follow the angular dependence of the systematic errors, provided they exceed the accuracy of the measurement. Table 2 gives the values for rhodium (at least 99·8%). No angular dependence of the lattice parameter is apparent, thus it is possible to say that within limits corresponding to the attained accuracy, systematic errors were in this case proportional to the supplement of the Bragg angle.

Table 2. *Lattice parameter of rhodium* ($t = 21._5$ °C.)

	Lines Cu K	$422\alpha_2$	$422\alpha_1$
72·0°	333β	3·80360 Å	3·80374 Å
65·2	$420\alpha_2$	3·80353	3·80363
64·9	$420\alpha_1$	3·80353	3·80363
63·7	422β	3·80361	3·80375
62·2	$331\alpha_2$	3·80361	3·80375
62·0	$331\alpha_1$	3·80359	3·80371
		Mean value	3·80364 Å ±0·00011 Å

Conclusions

The accuracy functions described make possible a very quick survey. They save much computational work by making it possible to preclude such cases that lead to a small accuracy, and to focus only on convenient cases. This is the chief significance of determining and tabulating the accuracy functions.

As to the ratio method, it is apparent that it is advantageous especially in those cases when the preparation of the specimen in other than plane form is difficult. The results which can be attained by it are satisfactory both with regard to cubic and to two-parameter lattices.

Summary

The paper gives some general relations concerning the accuracy functions for cubic and two-parameter lattices. The results of the lattice-parameter measurements (ruthenium, rhodium) with the aid of the ratio method

are interesting because an accuracy greater than 1 part in 10^4 has been attained through a simple experimental technique, whereby neither extrapolation procedures nor corrections of values directly measured were applied.

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Zur Brechungskorrektur bei Gitterkonstantenmessungen an Pulverpräparaten.

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Bei Gitterkonstantenmessungen ist eine Korrektur der gemessenen Glanzwinkel Θ_g erforderlich, durch die die Richtungsänderung der Röntgenstrahlen an den Kristalloberflächen und die Veränderung der auf Vakuum bezogenen Wellenlänge im Kristallinneren berücksichtigt wird.

$$\lambda_v = 2.d.\sin(\theta_g - \Delta\theta)\,. \qquad (1)$$

λ_v = Wellenlänge im Vakuum;
d = Netzebenenabstand;
θ_g = Glanzwinkel gemessen;
$\Delta\theta$ = Brechungs-Korrektur.

Diese Korrektur, der Kürze halber Brechungskorrektur, B.K., genannt, kann für Messungen an Einkristallen streng abgeleitet werden, wobei in erster Näherung die kinematische Theorie des Interferenzvorganges zum gleichen Ergebnis führt wie die dynamische Theorie. Experimentelle Untersuchungen ergaben weitgehende Übereinstimmung mit der Erwartung (Literaturangaben z.B. bei James (1954)).

Für Pulverpräparate ist die B.K. nicht exakt ableitbar, da keine definierte Lagebeziehung zwischen den Oberflächen der Pulverteilchen und dem Strahlengang besteht. Gelegentlich wird die B.K. des auf Einkristallmessungen bezogenen 'symmetrischen Falles' auch auf Messungen an Pulverpräparaten angewandt, Straumanis (1955).

$$\Delta\theta = 2\delta/\sin 2\theta;\ n = 1-\delta = \text{Brechungsindex};$$
$$\delta = 4{,}47.10^{-6}.\lambda^2/a^3.Z; \qquad (2)$$

λ = Wellenlänge in Å;
a = Elementarkante in Å;
Z = Zahl der Elektronen pro Elementarzelle.

Frohnmeyer & Glocker (1953) haben aber darauf hingewiesen, dass diese Korrekturgleichung für Pulverpräparate eventuell modifiziert werden muss. Nach Wilson (1940) umgeht man die Schwierigkeit der B.K. bei Pulverpräparaten, indem man an der durch Extrapolation gewonnenen Gitterkonstante nur die Veränderung der Wellenlänge im Kristallinneren berücksichtigt.

$$\Delta a/a = \delta\,. \qquad (3)$$

Da es mit neueren Messmethoden (z.B. mit Guinier-Kammern) möglich ist, Präzisionsmessungen, bezogen auf eine Eichsubstanz, schon im vorderen und mittleren Winkelbereich in Θ mit hoher Genauigkeit durchzuführen, scheint es von Interesse, die B.K. für Pulverpräparate und ihre Abhängigkeit von Θ genauer zu diskutieren.

Wegen der Unbestimmtheit von Gestalt und Grösse der Pulverteilchen lassen sich nur Grenzfälle untersuchen, aus denen sich ableiten lässt, welche Messunsicherheit die B.K. bei Gitterkonstantenmessungen verursacht.

D sei ein Mass für die Grösse der Pulverteilchen und μ der Absorptionskoeffizient der Substanz. Dann sollen Teilchen als 'sehr gross' gelten, wenn $D \gg 1/\mu$ ist. In diesem Fall trägt nur eine dünne Oberflächenschicht zur reflektierten Intensität bei. Setzt man zusätzlich voraus, dass die Teilchen von ebenen Flächen begrenzt sind, dann kann man annehmen, dass für einen einzelnen Interferenzvorgang an einem Mosaikbereich der eintretenden und der reflektierte Röntgenstrahl die gleiche Oberfläche schneidet. Für ein idealisiertes Modell lautet also die Frage, welche Abweichungen vom einfachen Bragg'schen Gesetzt treten auf, wenn die Oberfläche eines unendlich ausgedehnten, unendlich dicken Kristalles einen beliebigen Winkel mit dem Strahlengang bildet und im Mittel alle Orientierungen gleich wahrscheinlich sind? Entsprechend Fig. 1 ist die Oberflächenorientierung durch die Winkel α und φ gekennzeichnet. Das Snellius'sche Brechungsgesetz ergibt für vorgegebene Winkel α, φ, Θ als 1. Näherung in δ folgenden Ausdruck für die B.K.:

$$\Delta\theta = \tfrac{1}{2}\delta\,\{\operatorname{cotg}(\theta-\varphi) + \operatorname{cotg}(\theta+\varphi)\} + \delta.\operatorname{tg}\theta; \qquad (4)$$

Die Gleichung gilt nicht für extreme Oberflächenorientierungen mit $|\varphi|$ nahezu $=\Theta$, da die Entwicklung nach δ nur solange erlaubt ist, als die Winkel zwischen eintretendem oder reflektiertem Strahl und der Oberfläche grösser sind als $\varepsilon = \sqrt{(2\delta)}$ = Winkel der Totalreflexion. Um die Divergenz von Gl. (4) für $|\varphi| \to \Theta$ zu vermeiden, soll deshalb die Lagemöglichkeit der Oberflächennormale 0 auf $|\varphi| \leq \Theta - \eta$ begrenzt werden, wobei für η etwa $\varepsilon = \sqrt{(2\delta)}$ angenommen werden kann. Das ist erlaubt, da nachfolgend begründete Gewichtsfunktionen