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A Mathematical Technique for the Precision Determination of Lattice Parameters*

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A computer code has been developed for the precision determination of crystal lattice parameters, using the Hess method as a basis with the following modifications: (1) No approximations are made in the solution of the observation equation and (2) The method is extended to the hexagonal and orthorhombic crystal systems and to additional extrapolation functions. In the majority of the determinations, with randomly selected materials, the Hess approximation gave results comparable with the exact technique; however, because of certain restrictions the exact technique is recommended.

Introduction

The precision determination of lattice parameters is a powerful technique for basic studies of the solid state. Examples include the precise measurement of bond distances, true densities, thermal expansions, compressibilities, and solid-solution effects.

Graphical extrapolation methods for the elimination of systematic errors in lattice-parameter measurements have been treated by many investigators. Their correct usage has been discussed by Kempter (1959), and the most useful extrapolation functions tabulated as a function of Bragg angle.

Analytical methods have been discussed by Cohen (1935, 1936*a*, 1936*b*) and Hess (1951). These methods are more readily applicable than extrapolation methods to non-cubic crystal systems, but the complexity of the calculations necessitates the use of a computing machine. Of the two analytical methods, the Hess method is preferable since it assigns statistical weights to the observed points. This weighting is a necessity since the weighting function increases tremendously as the Bragg angle approaches 90° θ.

For the cubic system, using a Debye–Scherrer or symmetrical back-reflection focusing camera, Hess started his fitting procedure with the following general equation expressing the function F.

$$F = A_0\alpha + K_0\delta - \gamma , \qquad (1)$$

where

$A_0 = 1/a_0^2$; $a_0 =$ the lattice parameter;

$\alpha = \frac{1}{2}\lambda^2 n^2(h^2+k^2+l^2)$; $\lambda =$ wave length,
                                           $n =$ an integer,
                                           $hkl =$ Miller indices;

$K_0 =$ the 'drift constant';

$\delta = \Phi \sin \Phi$, the error term, which assumes
          $\Delta\Phi \propto \Phi$, where $\Phi = \pi - 2\theta$;

$\gamma = 1 + \cos \Phi = 2 \sin^2 \theta$.

By setting K_0 equal to zero, Hess calculated values of F_0 at every observed point and also arrived at the weighting function $\operatorname{cosec}^2 \Phi$. Using Deming's (1943) method, he solved for A_0 and K_0 and then for a_0. Hess also treated the tetragonal lattice and the flat-film symmetrical back-reflection camera.

The following general equations apply for the crystal systems treated in this article, where a_0, b_0, and c_0 are the lattice parameters, $T_1 = 1/a_0^2$ (except for the hexagonal system), $T_2 = K_0$, the 'drift constant', $T_3 = 1/c_0^2$, $T_4 = 1/b_0^2$, $x_2 =$ the error term, $x_3 = \frac{1}{2}\lambda^2 l^2$, $x_4 = \frac{1}{2}\lambda^2 k^2$, and $y = \gamma$. (See equation (1) for the definition of λ and hkl). The integer n is omitted since it is equal to unity.

Cubic
$$F = T_1 x_1 + T_2 x_2 - y , \qquad (2)$$
where $x_1 = \frac{1}{2}\lambda^2(h^2 + k^2 + l^2)$.

Tetragonal
$$F = T_1 x_1 + T_3 x_3 + T_2 x_2 - y , \qquad (3)$$
where $x_1 = \frac{1}{2}\lambda^2(h^2 + k^2)$.

Hexagonal
$$F = T_1 x_1 + T_3 x_3 + T_2 x_2 - y , \qquad (4)$$
where $T_1 = 4/(3a_0^2)$; $x_1 = \frac{1}{2}\lambda^2(h^2 + hk + k^2)$.

Orthorhombic
$$F = T_1 x_1 + T_3 x_3 + T_4 x_4 + T_2 x_2 - y , \qquad (5)$$
where $x_1 = \frac{1}{2}\lambda^2 h^2$.

The error term x_2 is selected according to the measurement geometry and the experimental techniques used (Kempter, 1959). By definition $x_2 = \Delta\Phi \sin \Phi/K_0$, where $\Phi = (\pi - 2\theta)$.

For the symmetrical back-reflection focusing camera, the systematic errors in $\Delta a_0/a_0$ are proportional to $\varphi \tan \varphi$, where $\varphi = (90° - \theta) = \frac{1}{2}\Phi$. Therefore, $\delta = K_0\Phi \sin \Phi/K_0 = \Phi \sin \Phi$. In terms of back-reflection ring diameter, s, and camera diameter, D,

$$x_2 = (s/2D) \sin (s/2D) . \qquad (6)$$

For the Debye–Scherrer camera, the systematic errors in $\Delta a_0/a_0$ are proportional to $\varphi \tan \varphi$, $\cos^2 \theta$, or $\frac{1}{2}[(\cos^2 \theta/\sin \theta) + (\cos^2 \theta/\theta)]$ depending upon the experimental techniques used. Therefore, $x_2 = \Phi \sin \Phi$, $\sin^2 2\theta$, or $\sin^2 2\theta[(1/\sin \theta) + (1/\theta)]$, respectively. In terms of s and D these become:

$$x_2 = \frac{s}{D} \sin \frac{s}{D} . \qquad (7)$$

$$x_2 = \sin^2 \left(\pi - \frac{s}{D}\right) . \qquad (8)$$

$$x_2 = \sin^2 \left(\pi - \frac{s}{D}\right) \left[\frac{1}{\sin\left(\frac{\pi}{2} - \frac{s}{2D}\right)} + \frac{1}{\left(\frac{\pi}{2}\right) - \frac{s}{2D}}\right] . \qquad (9)$$

For the diffractometer, the systematic errors in $\Delta a_0/a_0$ caused by displacement of the specimen surface from focusing circle are proportional to $\cos \theta \cot \theta$. Therefore, $x_2 = \sin \theta \cos^2 \theta$. Since 2θ is the measurement made in this method, the final equation becomes:

$$x_2 = \sin \frac{2\theta}{2} \cos^2 \frac{2\theta}{2} . \qquad (10)$$

Other error terms may of course be substituted and/or additional error terms added by solving for $\Delta\Phi$ and then for x_2. The angles in equations (6) through (9) are in radians.

No attempt was made to extend the code to the monoclinic and triclinic crystal systems because of their limited usefulness; the rhombohedral system may of course be indexed on hexagonal axes.

Mathematical treatment

The problem is to determine estimates of the parameters for equations (2), (3), (4) and (5). A general equation, which includes (2), (3), (4), and (5), can be written:

$$y_e = \sum_{i=1}^{m} T_i x_{ie} , \qquad (11)$$

where $e = 1, \ldots, N$; $N =$ number of experimental data points and $m = 2$ for the cubic system, $m = 3$ for the tetragonal and hexagonal systems, and $m = 4$ for the orthorhombic. The variables y_e and x_{2e} are both functions of θ.

Estimates of the parameters, T, can be obtained from the experimental data by the method of least-squares. Minimizing the function

$$Q = \sum_{e=1}^{N} W_e F_e^2 , \qquad (12)$$

where

$W_e =$ the weight associated with each F_e

$$F_e = \sum_{i=1}^{m} a_i x_{ie} - y_e$$

$a_i =$ the least-squares estimate of T_i

will give the weighted least-squares estimate of the parameters.

The weighting function (Hald, 1952), W_e, used is inversely proportional to the variance, $\sigma^2_{F_e}$ of F_e. One can show by using error propagation that

$$\sigma^2_{F_e} = \left(\frac{\partial F_e}{\partial \theta_e}\right)^2 \sigma^2_{\theta_e} . \qquad (13)$$

The random error of θ_e is assumed constant* and acts as a proportionality constant which can be ignored in the analysis, so that

$$W_e = \frac{1}{\left(\sum_{i=1}^{m} \frac{\partial x_{ie}}{\partial \theta_e} a_i - \frac{\partial y_e}{\partial \theta_e}\right)^2} \qquad (14)$$

Because W_e is a function of the parameters, an iterative method described by Deming (1943) is used to minimize Q. With a set of initial estimates for the parameters, a_i, the iteration procedure continually

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* The reading of a large number of diffraction films have shown this assumption to be valid.

computes corrections to these estimates until such corrections are deemed 'sufficiently small'.

Estimates of the standard deviations of the parameters can be shown to be

$$\text{S.D.}_{\cdot a_i} = \left(\frac{Q_F}{N-m}\cdot x^{-1}{}_{ii}\right)^{\frac{1}{2}},$$ (15)

where Q_F = the value of Q obtained from the last iteration, and $x^{-1}{}_{ii}$ is the ii element of the inverse of the matrix

$$x_{ij} = \left\|\begin{array}{ccc} \sum\limits_{e=1}^{m} W_e x^2{}_{1e} \dots & \sum\limits_{e=1}^{m} W_e x_{1e} x_{me} \\ \vdots & \vdots \\ \sum\limits_{e=1}^{m} W_e x_{1e} x_{me} \dots & \sum\limits_{e=1}^{m} W_e x^2{}_{me} \end{array}\right\|.$$ (16)

The standard deviation of the parameter(s) is used in determining confidence limits and also in testing to see if the parameters are significantly different from zero (Hald, 1952).

It should be pointed out that stopping after the first iteration, as Hess (1951) has suggested, is not theoretically sufficient when computing the standard deviation of the parameters. Although K_0 values are quite small, it has been shown that there exist some K_0's which are statistically significantly different from zero. Hence, using zero as the approximation for K_0 will not always give the statistically best estimate of the $\|x_{ij}\|^{-1}$ matrix, which one uses in the computation of the standard deviation. It is recommended that if one uses such an approximation, i.e., setting K_0 equal to zero and stopping after the first iteration, the $\|x_{ij}\|^{-1}$ matrix and the Q function should be computed with the new approximations before computing the standard deviation of the parameters.

A useful subjective technique to determine the 'reasonableness' of the fit is to order the y observed values and compare them with the y's which have been calculated from the x's and the fitted parameters. By forming y observed minus y calculated, and examining the signs of these differences, one can infer that the fit is reasonable if the signs are randomly distributed.

Although the iterative technique should be carried out until convergence is reached when using high-speed computers, it is of interest to those who do not have such facilities to evaluate an approximation technique for determining lattice parameters. Using K_0 equal to zero and approximations for the lattice parameters good to three digits and stopping after the first iteration gave excellent approximations for the lattice parameters of the materials we tested. Just how well this approximation does compared to the convergent iterative technique is a function of K_0 and the range of θ used.

Results and discussion

The results for a number of representative examples of the problems and cases run are tabulated in Table 1 in order of increasing mass absorption coefficients (μ_m in cm.^{2}g.$^{-1}$). The cubic, tetragonal, hexagonal, and orthorhombic crystal systems are designated as problems 1, 2, 3, and 4 respectively; the error equations 6, 7, 8, 9, and 10 are designated as cases $1A$, $1B$, 2, 3, and 4 respectively. K_0 is the 'drift constant' and a_0, b_0, and c_0 are the lattice parameters in Ångström units at 25 °C.; σ is the precision of the parameter expressed as the standard deviation.

Each example was computed by two methods. The first, designated by AP, was an approximate technique, i.e., setting K_0 equal to zero and stopping after the first iteration. The standard deviation of the parameters were computed with the first $\|x_{ij}\|^{-1}$ matrix and the correct Q function. The second method, designated by EX, was an exact technique, i.e., continuous iteration until convergence was reached.

International Union of Crystallography standard specimens are designated I.U.C. Copper radiation (nickel filtered) was used in all cases, except for Li and UC, where cobalt radiation (iron filtered) and chromium radiation (vanadium filtered) were used, respectively. The lattice parameters are not corrected for refraction. Lonsdale's (1950) wavelengths were used in all computations. All specimens, except Li in the form of wire, were −325 mesh and were not diluted. Debye–Scherrer specimens were run in 0·3 mm. diameter Lindemann glass capillaries; back-reflection specimens were run on rubber–cement–coated cardboard. Case $1A$ films were read by three readers, thus tripling the number of points. For numbers 20, 21, and 22, only very high Bragg angle reflections were measured. For cases 2 and 3, a film should properly be corrected for film shrinkage; in order to show the effect of this correction, the film for number 21 has been corrected for shrinkage. The film for beta tin is unique in that the shrinkage correction factor is unity. The lattice parameter obtained for number 7 has been corrected only for the specimen-surface displacement error.

It was noted that of the Debye–Scherrer films examined, the absolute value of K_0 was highest for case 2, lowest for case 3, and intermediate for case $1B$. It can be readily shown that K_0 is actually an analytical systematic-errors constant which is related to the extrapolation systematic-errors constant K'' by a simple relationship. Using the cubic system and case 1 as an example: The error equation is $\Delta a_0/a_0 = K' \varphi \tan\varphi$, where $\varphi = (\pi/2 - \theta)$ radians. In practice, values of the lattice parameter are plotted against corresponding values of $\varphi \tan\varphi$ and a linear extrapolation is carried out to $\varphi\tan\varphi = 0$. Therefore, $a = K''\varphi\tan\varphi + a_0$, where K'' is the slope and a_0 is the y-intercept. Substituting Δa_0 for $(a - a_0)$ and dividing the equation by a_0, we obtain:

Table 1

No.	Problem	Case	Material	μ_m	No. pts.	K_0	σ_{K_0}	a_0	σ_{a_0}	b_0	σ_{b_0}	c_0	σ_{c_0}
1AP	1	1B	Li	1-13	3	−0·000587	0·000373	3·509553	0·000173				
1EX	1	1B	Li	1-13	3	−0·000587	0·000373	3·509553	0·000173				
2AP	1	1A	I.U.C. Diamond	5-5	12	−0·002803	0·000089	3·567145	0·000061				
2EX	1	1A	I.U.C. Diamond	5-5	12	−0·002803	0·000089	3·567145	0·000061				
3AP	1	1A	I.U.C. Silicon	60-3	18	−0·002832	0·000106	5·430482	0·000055				
3EX	1	1B	I.U.C. Silicon	60-3	18	−0·002832	0·000106	5·430482	0·000055				
4AP	1	1B	I.U.C. Silicon	60-3	18	−0·000795	0·000172	5·430502	0·000089				
4EX	1	1B	I.U.C. Silicon	60-3	18	−0·000795	0·000172	5·430502	0·000089				
5AP	1	2	I.U.C. Silicon	60-3	18	−0·000935	0·000196	5·430527	0·000091				
5EX	1	2	I.U.C. Silicon	60-3	18	−0·000934	0·000196	5·430527	0·000091				
6AP	1	3	I.U.C. Silicon	60-3	18	−0·000454	0·000098	5·430498	0·000088				
6EX	1	3	I.U.C. Silicon	60-3	18	−0·000454	0·000098	5·430498	0·000088				
7AP	1	4	Norelco Std. Silicon	60-3	4	−0·001083	0·001382	5·429923	0·000484				
7EX	1	4	Norelco Std. Silicon	60-3	4	−0·001083	0·001382	5·429923	0·000484				
8AP	3	2	ZrB₂ I	116	15	−0·011948	0·004668	3·169989	0·001477			3·531080	0·003796
8EX	3	2	ZrB₂ I	116	15	−0·011961	0·004674	3·169995	0·001491			3·531066	0·003824
9AP	3	3	ZrB₂ I	116	15	−0·005728	0·002199	3·169898	0·001456			3·530827	0·003727
9EX	3	3	ZrB₂ I	116	15	−0·005728	0·002199	3·169899	0·001458			3·530824	0·003731
10AP	3	1B	ZrB₂ II	116	19	−0·002361	0·000118	3·169227	0·000065			3·530773	0·000160
10EX	3	1B	ZrB₂ II	116	19	−0·002361	0·000118	3·169227	0·000065			3·530773	0·000160
11AP	3	2	ZrB₂ II	116	19	−0·003133	0·000160	3·169261	0·000067			3·530910	0·000165
11EX	3	2	ZrB₂ II	116	19	−0·003133	0·000160	3·169261	0·000067			3·530910	0·000165
12AP	3	3	ZrB₂ II	116	19	−0·001360	0·000068	3·169223	0·000065			3·530771	0·000160
12EX	3	3	ZrB₂ II	116	19	−0·001360	0·000068	3·169223	0·000065			3·530771	0·000160
13AP	3	1A	ZrB₂ II	116	30	−0·004501	0·000107	3·169092	0·000011			3·530891	0·000058
13EX	3	1A	ZrB₂ II	116	30	−0·004501	0·000107	3·169092	0·000011			3·530891	0·000058
14AP	3	1B	NbB₂	125	6	−0·002265	0·001157	3·101700	0·001782			3·293083	0·000180
14EX	3	1B	NbB₂	125	6	−0·002266	0·001156	3·101700	0·001782			3·293083	0·000180
15AP	3	2	NbB₂	125	6	−0·003823	0·002077	3·102673	0·002491			3·293201	0·000201
15EX	3	2	NbB₂	125	6	−0·003825	0·002074	3·102675	0·002487			3·293201	0·000201
16AP	1	1A	I.U.C. Tungsten	171	9	−0·002830	0·000095	3·165073	0·000037				
16EX	1	1A	I.U.C. Tungsten	171	9	−0·002830	0·000095	3·165073	0·000037				
17AP	4	1A	Yellow HgO	207	8	−0·003073	0·000627	6·610087	0·000304	5·519638	0·001479	3·520338	0·000439
17EX	4	1A	Yellow HgO	207	8	−0·003073	0·000628	6·610087	0·000304	5·519638	0·001479	3·520337	0·000439
18AP	2	3	Beta Tin	265	18	−0·001112	0·000098	5·831777	0·000101			3·181816	0·000156
18EX	2	3	Beta Tin	265	18	−0·001112	0·000098	5·831777	0·000101			3·181816	0·000156
19AP	2	1B	Beta Tin	265	18	−0·001943	0·000171	5·831784	0·000102			3·181821	0·000156
19EX	2	1B	Beta Tin	265	18	−0·001943	0·000171	5·831784	0·000102			3·181821	0·000156
20AP	2	3	Beta Tin	265	8	−0·001151	0·000188	5·831794	0·000094			3·181787	0·000126
20EX	2	3	Beta Tin	265	8	−0·001151	0·000188	5·831794	0·000094			3·181787	0·000126
21AP	1	3	ThO₂	289	6	−0·001178	0·000207	5·597539	0·000067				
21EX	1	3	ThO₂	289	6	−0·001178	0·000207	5·597539	0·000067				
22AP	1	3	ThO₂	289	6	−0·000221	0·000216	5·597550	0·000070				
22EX	1	3	ThO₂	289	6	−0·000221	0·000216	5·597550	0·000070				
23AP	1	1A	ThO₂	289	36	−0·003090	0·000063	5·597482	0·000027				
23EX	1	1A	ThO₂	289	36	−0·003090	0·000063	5·597482	0·000027				
24AP	1	3	UC	767	3	0·000972	0·000279	4·960778	0·000558				
24EX	1	3	UC	767	3	0·000972	0·000279	4·960778	0·000557				

$$\Delta a_0/a_0 = (K''/a_0)\varphi \tan \varphi, \quad \text{and} \quad K' = K''/a_0 . \quad (17)$$

By differentiation of the Bragg equation:

$$\Delta a_0/a_0 = -\cot \theta \Delta\theta = -\tan \varphi \Delta\varphi . \quad (18)$$

And since $K_0 = \Delta\Phi/\Phi = \Delta\varphi/\varphi$, and so $\Delta\varphi = K_0\varphi$:

$$\Delta a_0/a_0 = -K_0\varphi \tan \varphi = K'\varphi \tan \varphi . \quad (19)$$

$$\therefore K_0 = -K' = -K''/a_0 . \quad (20)$$

Similarly it can be shown that $K' = K''/a_0$ for all cases, and that $K_0 = -K''/2a_0$, $-K''/4a_0$, and $-2K''/a_0$ for cases 2, 3, and 4 respectively.

Since many factors influence the systematic-errors constant, it is very difficult to predict its value. Reference to Table 1 shows that a prediction *cannot* be made on the assumption that absorption is the overriding cause of systematic error.

An examination of Table 1 shows that, in general, the Hess method is an excellent approximation for the lattice parameters and K_0 values for the problems and cases treated. All the lattice parameters are rounded off at the sixth decimal place. [It is standard practice to round off precision lattice parameters to five decimal places (since the wavelengths used have five decimal places) *after* the refraction correction has been added on.] It should be noted that as the absolute value of K_0 increases, the approximate lattice parameters diverge from the exact values; the a_0 and c_0 values for number 8 illustrate this divergence. The divergence also increases as the Bragg-angle range increases, as pointed out in the mathematical discussion. Thus, in using the approximate method, one must also be selective in choosing the Bragg angle range. Cases 1 and 2 are properly applied to reflections greater than 57° and 60° θ, respectively; however, cases 3 and 4 have wide ranges of applicability. All the Bragg angles used in the preparation of Table 1 were back-reflection angles.

Further examination of Table 1 illustrates the approximate method of computing standard deviations, i.e., using the first $\|x_{ij}\|^{-1}$ matrix obtained, is very good. It should be noted again that as the absolute value of K_0 increases, the approximation to the standard deviation of the parameters becomes poor (see number 8). It must be remembered that approximations made in this manner are only estimates for the standard deviations computed exactly, hence smaller standard deviations obtained by the approximation technique compared to the iterative-convergence technique does not imply that one gets smaller errors in the lattice parameters by using the approximation technique.

It is concluded that, in general, a single iterative technique (such as the Hess method) is an excellent approximation; however, in view of certain restrictions, a convergent iterative technique is recommended. The advantage of the latter technique is that it yields the best estimate of the lattice parameter(s) and the standard deviation(s), regardless of the error function used.

All computations in Table 1 were done with an IBM 704 Fortran code written by one of the authors (R. E. Vogel).

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