A New Least-squares Method for Determination of Lattice Parameters from Powder X-ray Diffraction Data

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A new least-squares method is described, which can be applied to the determination of lattice parameters in cubic, tetragonal, orthorhombic and hexagonal crystals. This procedure is constructed by a combination of the Cohen's analytical method and a method proposed by Lutts, being characteristic of using any pair of diffraction lines. In order to eliminate partially the influence of the systematic errors, a modified observation equation is used effectively in the present method. The following advantages are considered:

1. The number of “unknown parameters” decreases by one in comparison with the Cohen’s method,
2. Observation equations greatly increase in number to be adequate in the least-squares treatment, and
3. For cubic crystals, it is not necessary to use the least-squares method.

Thus, the present method allows us to calculate the lattice parameters more easily and rapidly than the Cohen’s method.

The lattice parameters of a Pb-15at%Bi alloy (cubic) and a pure In (tetragonal) were determined by the present method. For orthorhombic crystals, a comparison of procedures was made. The results were found to be almost the same as those by Cohen’s method.

(Received August 15, 1986)

Keywords: lattice parameter, powder X-ray diffraction, least-squares method, cubic, tetragonal, orthorhombic, hexagonal, axial ratio, Cohen’s method, analytical extrapolation method

1. Introduction

It goes without saying that the accurate determination of the lattice parameters is very important not only in determining crystal structures but also in understanding some metallurgically fundamental problems such as the factors leading semiconductivity and magnetic properties in metals and alloys. Many attempts have been done to obtain accurate lattice parameters easily and rapidly. Under the present conditions, it is probably more satisfactory to use the analytical method in cases of crystals of low symmetry, for example, an analytical extrapolation method (Cohen’s method(1,2)) as well as a method modified by Hess(3). But for all ordinary work on cubic crystals the graphical method is preferred for simplicity and for the facility with which reflection can be suitably weighted. Recently, Lutts(4,5) has proposed a simple method for the precise determination of the lattice parameters from X-ray powder patterns of trigonal, tetragonal and orthorhombic crystals: In his procedure, the axial ratios are calculated first to eliminate partially the influence of systematic errors in the square of the axial ratios, and then from those values each lattice parameter is deduced. This method, however, is not applicable to cubic crystals. Moreover, for the orthorhombic crystals the results obtained by this procedure differ from the values calculated by Cohen’s method, in which the basic analytical extrapolation is extended to a least-squares treatment in order to reduce the effect of random errors in the initial data. Accordingly, the present authors have

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tried to modify this calculation procedure using a new least-squares method combined with a correction function $F(\theta_i)$ based on $\cos^2 \theta$ or Nelson-Riley extrapolation function. This modification is essentially the same as the Cohen's method, except for the use of different observation equations which are given for any pair of diffraction lines. However, this modification has a great advantage in that the number of "unknown parameters" to be used is smaller by one than that of the Cohen's method.

In this paper, a very simple example is given for the precise determination of lattice parameters of cubic and tetragonal crystals. Also, a comparison between this modified method and other methods was made in several cases by using the same experimental data. The calculations were done with a 16 bits personal computer using programs written in BASIC.

II. Principle of Procedure

In this section, the outline of procedure is described. The quadratic form of the Bragg equation for orthorhombic crystals is given by

$$\sin^2 \theta_i = (\lambda^2/4 \alpha^2)(h_i^2 + k_i^2 H + l_i^2 L), \quad (1)$$

where $\theta_i$ is the usual Bragg angle for the diffraction line $i$, being an error-free or true angular position in a hypothetical case in which no sources of errors are present, $\lambda$ is the wavelength and $h_i, k_i, l_i$ are reflection indices. $H$ and $L$ are given in the following manner, using lattice parameters $a, b$ and $c$,

$$H = a^2/b^2 \quad \text{and} \quad L = a^2/c^2. \quad (2)$$

As is well known, angular positions of any diffraction lines are influenced by several sources of systematic errors. In most cases, a diffraction line appears at a slightly larger angle than $\theta_i$ and all errors, when very thin specimens and fine X-ray beams are used, decrease continuously as the measured diffraction angle $\theta_i$ increases and finally vanish when $\theta_i$ approaches $\pi/2$. Accordingly, in order to eliminate systematic errors inherent in all the present types of precision cameras, a correction term, $DF(\theta)$, due to the net effect of all the systematic errors, is introduced here on the basis of the analytical treatment proposed by Cohen\(^{(1, 2)}\), which is defined in the next relation,

$$\sin^2 \theta_i = \sin^2 \theta_0 + DF(\theta_i). \quad (3)$$

Here $\theta_i$ is a measured angular position of a diffraction line $i$, and $D$ (hereafter, referred to as the drift constant\(^{(1)}\)) is a constant for any particular films, but may vary from film to film, so that the numerical value of the constant $D$ for a particular film is unknown at first. According to Hess\(^{(3)}\), $D$ is always less than $\pm 0.02$ and usually less than $\pm 0.005$, so that the correction term $DF(\theta_i)$ is always small enough to justify the approximations made in developing eq. (3). The correction function $F(\theta_i)$ will be described in the section III, together with practical exercises.

Here, eq. (1) is rewritten in terms of the lattice constant $a$ and the reflection indices, which gives an "observation equation" into the form

$$\sin^2 \theta_i = (\lambda^2/4a^2)(h_i^2 + k_i^2 H + l_i^2 L) + DF(\theta_i). \quad (4)$$

Let's consider two kinds of diffraction lines, $i$ and $j$, having reflection indices $h_i, k_i, l_i$ and $h_j, k_j, l_j$ and the Bragg angles $\theta_i$ and $\theta_j$, respectively. When the same characteristic wavelength is employed to measure the angular positions of both line $i$ and line $j$, the ratio of two equations of type (4),

$$\frac{\sin^2 \theta_j}{\sin^2 \theta_j} = \frac{h_j^2 + k_i^2 H + l_j^2 L + (4a^2/\lambda^2)DF(\theta_j)}{h_i^2 + k_i^2 H + l_i^2 L + (4a^2/\lambda^2)DF(\theta_i)}$$

leads to the next relation,

$$\left(\sin^2 \theta_i h_i - \sin^2 \theta_j k_j\right) H$$

$$+ \left(\sin^2 \theta_i l_i - \sin^2 \theta_j l_j\right) L$$

$$+ \left(\sin^2 \theta_i F(\theta_i) - \sin^2 \theta_j F(\theta_j)\right) A$$

$$+ \sin^2 \theta_i h_i^2 - \sin^2 \theta_i h_i^2 = 0,$$  \quad (5)

employing the substitution

$$A = (4a^2/\lambda^2)D. \quad (6)$$

This type of equation is given for any pair of diffraction lines, where it is assumed that there are no accidental errors. In practical experiments, this equation still includes residuals for accidental errors, which will be discussed after in comparison with the Cohen's method.
Considering the influence of systematic errors, it is evident that the errors in $H$, $L$ and $A$ will be the smallest when: 1) two diffraction lines, $i$ and $j$, appear at very high Bragg angles and 2) the angular separation between the two lines is not too large. In general, these conditions can be satisfied, when a sufficient number of available diffraction lines are observed densely at higher angles.

When $N$ diffraction lines for various sets of $hkl$ are used, we obtain $N C_2$ observation equations of type (5), and by applying the least-squares treatment to solve these $N C_2$ equations, it is possible to calculate the most probable values of $H$, $L$ and $A$. However, these values do not give error-free lattice parameters directly. This point is different from the Cohen's method according to which the error-free values, $a_0$, $b_0$ and $c_0$, can be deduced directly. The determination of the error-free parameters will be described below.

Here, several actual procedures are described. Particularly, for tetragonal crystals $H$ is unity and for cubic crystals both $H$ and $L$ are unity. Thus the number of unknown parameters decreases by one and by two, respectively. For cubic crystals the parameter $A$ can be determined as the mean value, because the observation equation used has only one parameter and then the least-squares treatment gives us the same value as the mean value. On the contrary, the calculation procedure of lattice parameters for orthorhombic crystals is as follows: Firstly, in order to obtain the most probable values of $H$, $L$ and $A$, observation equations of type (5) are solved by applying the least-squares treatment, and using the obtained value of $A$, we can calculate the drift constant $D$ by eq. (6). Here, we have no choice but to use an expedient value of lattice parameter $a$, which is calculated with an angular position of a diffraction line observed at the highest Bragg angle. This approximation seems adequate, because the drift constant is usually so small that a little variation of $a$-value does not produce any large deviation in the results obtained\(^{(3)}\). Secondly, the value of lattice parameter $a_i$ is determined for each diffraction line by the following relation:

$$a_i = (\lambda/2) \sqrt{(h^2 + k^2 H + l^2 L) [\sin^2 \theta_i - DF(\theta_i)]},$$

where most probable values of $H$ and $L$ are used together with a given function $F(\theta_i)$ described in the next section. By using this $a_i$ value, lattice parameters $b_i$ and $c_i$ are determined from eq. (2). However, it should be noted here that these calculated lattice parameters, $a_i$, $b_i$ and $c_i$, for each diffraction line are not the true values, because the used $H$, $L$ and $D$ have slight differences from the true values, and also a measured position of each diffraction line involves accidental errors. Accordingly, error-free values of lattice parameters, $a_0$, $b_0$ and $c_0$, can be obtained by averaging these values weighted by a proper function of $\theta$ for each diffraction line. In the present study, considering that $\Delta a/a = -\Delta \theta/\tan \theta_i$, we multiply $a_i$ by $\tan \theta_i$ so that many diffraction lines observed at small angles can be used for calculation under equivalent weighting of accuracy. The same weighting factor, $\tan \theta_i$, has already been used by Otte and Esquivel\(^{(6)}\), although they had used the factor in the technique of least-squares treatment. Finally, the error-free values, $a_0$, $b_0$ and $c_0$, are deduced by the next relations,

$$a_0 = \sum_i a_i \tan \theta_i / \sum_i \tan \theta_i,$$

$$b_0 = \sum_i b_i \tan \theta_i / \sum_i \tan \theta_i,$$

and

$$c_0 = \sum_i c_i \tan \theta_i / \sum_i \tan \theta_i.$$  \hspace{1cm} (8)

To the case of hexagonal or trigonal crystal, or to the case in which different characteristic X-rays are used, this procedure is also applicable with a small modification (Appendix).

III. Applications and Comparison of the Procedures

In a practical calculation, we must define a proper function $F(\theta_i)$ to eliminate systematic errors for any type of precision cameras. In the present study, a correction function based on the $\cos^2 \theta$ or Nelson-Riley extrapolation function, namely,
\[ F_1(\theta) = \sin^2 2\theta \]

or

\[ F_2(\theta) = \sin^2 2\theta (1/\sin \theta + 1/\theta) \quad (9) \]

was used. A Pb-15 at% Bi alloy and a pure indium metal (99.99%) were measured by using a Debye-Scherrer camera with CuK\(\alpha\) radiation. In a higher angular region, diffraction lines were separated into two lines with K\(_{\alpha1}\) and K\(_{\alpha2}\) radiations. Only the diffraction lines due to K\(_{\alpha1}\) radiation were used for calculation of observation equations. The results from the alloy and the metal are shown in Table 1 and Table 2, respectively. For the Pb-15 at% Bi alloy, a lattice parameter obtained from the mean value of the parameter \(A\) seems to be in good agreement with the data reported by Hayashi\(^7\). For the indium metal, lattice parameters obtained by the present method are in good agreement with the values obtained by the Cohen's method, except the case where 9 diffraction lines and the Nelson-Riley extrapolation function were employed.

Lutts\(^5(9)\) carried out precise experiments on lattice parameters of trigonal (\(\alpha\)-quartz) and orthorhombic (TiPt) crystals. We calculated the lattice parameters on the basis of their experimental data, in order to compare the accuracy between the present method and the other methods. Results are shown in Tables 3 and 4. In both cases, it is found that lattice parameters obtained by the present method are much closer to those by the Cohen's method than to the results by a procedure of Lutts, and that both correction functions, \(\cos^2 \theta\) and the Nelson-Riley extrapolation function, give almost the same results. This may suggest that

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**Table 1** Comparison among lattice parameter values of a Pb-15 at% Bi alloy (cubic) obtained by different methods.

| Correction function | Number of peaks | Lattice parameter (nm) |
|---------------------|-----------------|------------------------|
| Present method      |                 |                        |
| \(F_1(\theta)\)     | 5 (2\(\theta\) > 98°) | 0.4968                 |
| \(F_2(\theta)\)     | 5               | 0.4968                 |
| \(F_1(\theta)\)     | 7 (2\(\theta\) > 85°) | 0.4967                 |
| \(F_2(\theta)\)     | 7               | 0.4967                 |
| \(F_1(\theta)\)     | 12 (2\(\theta\) > 31°) | 0.4967                 |
| \(F_2(\theta)\)     | 12              | 0.4967                 |
| Cohen's method      |                 |                        |
| \(F_1(\theta)\)     | 5               | 0.4066                 |
| \(F_2(\theta)\)     | 7               | 0.4966                 |
| \(F_2(\theta)\)     | 12              | 0.4967                 |
| Only one peak       | 620 ref. (2\(\theta\) = 157.72°) | 0.4965                 |
| Reference           |                 |                        |
| Hayashi\(^7\)       | Pb-15.33 at% Bi | 0.49694                |
|                     | Pb-13.62 at% Bi | 0.49674                |

**Table 2** Comparison among lattice parameter values of an indium metal (tetragonal) obtained by different methods.

| Correction function | Number of peaks | Lattice parameter (nm) |
|---------------------|-----------------|------------------------|
| Present method      |                 |                        |
| \(F_1(\theta)\)     | 5\(\theta > 140°\) | 0.45975                 |
| \(F_2(\theta)\)     | 5               | 0.45975                 |
| \(F_1(\theta)\)     | 9\(\theta > 102°\) | 0.45974                 |
| \(F_2(\theta)\)     | 9               | 0.45966                 |
| Cohen's method      |                 |                        |
| \(F_1(\theta)\)     | 5               | 0.45973                 |
| \(F_2(\theta)\)     | 9               | 0.45972                 |
| Reference           |                 |                        |
| Pearson\(^9\)       |                 |                        |
|                     |                 | 0.45981                 | 0.49469                |
the present procedure is modified more effectively than the Lutts’s method, being comparable with the Cohen’s method.

### IV. Discussion of the Weighting Factor for the Observation Equation

In a practical calculation, the weighting factor in the least-squares treatment is usually taken into consideration. Therefore, in order to check if reasonable weighting factors are used in the present computer calculation process, it is necessary to discuss the present weighting factor in comparison with that of the Cohen’s method.

First, we consider the expression of residual errors in the present method. The residual errors should be discussed on the basis of the observation equation expressed by eq. (5), because they are due to errors caused by \( H, L, A, \theta_i \), and \( \theta_j \). However, it is not easy to induce the residual errors directly, because the expression of the present observation equation is given for any pair of diffraction lines and is not the same as that of the Cohen’s method. Accordingly, we rewrite eq. (5) to compare with the Cohen’s treatment, in which a residual error \( \nu \) for a diffraction line \( i \) is given by

\[
\nu_i = \sin^2 \theta_0 + D F(\theta) - \sin^2 \theta_i.
\]

Using eqs. (3) and (4), eq. (5) is expressed by

\[
(4 a^2 / \lambda^2)[\sin^2 \theta_i \{\sin^2 \theta_0 + D F(\theta_i)\} - \sin^2 \theta_i \{\sin^2 \theta_0 + D F(\theta_j)\}] = 0.
\]

It goes without saying that, when no source of experimental errors exists, eq. (11) is always true. However, in practical cases, where several sources of systematic errors are associated with experimental results, eq. (11) is not true any more. Therefore, according to the Cohen’s concept concerning residual errors, the present residual error \( \nu_{ij} \) is given by

\[
\nu_{ij} = (4a^2 / \lambda^2)[\sin^2 \theta_i \{\sin^2 \theta_0 + D F(\theta_i)\} - \sin^2 \theta_j \{\sin^2 \theta_0 + D F(\theta_j)\}].
\]

Using the \( \nu \)’s for two diffraction lines \( (\nu_i \) and \( \nu_j) \), \( \nu_{ij} \) can be expressed by the following equation,

\[
\nu_{ij} = (4a^2 / \lambda^2)(\sin^2 \theta_i \nu_i - \sin^2 \theta_j \nu_j).
\]

Therefore, when all combinations of paired diffraction lines of \( i \) and \( j \) are used, the sum of
equally weighted squares of the residual errors, $S$, should be minimized, which is given by

$$S = \sum_i \sum_j v_i^2$$

$$\div (4a^2/\lambda^2)^2 \sum_i \sum_j (\sin^2 \theta_i v_i^2 + \sin^4 \theta_i v_j^2). \quad (i < j).$$

(14)

Here the sum of the cross terms, $v_i v_j$, was neglected according to a usual least-squares treatment, because $v_i$ usually gives positive or negative values for any diffraction line. This procedure is quite similar to Cohen's procedure$^{(1)(2)}$, where is minimized the sum of squares of residuals, $\sum_i v_i^2$. Since $\sin^2 \theta$ is not too different from unity in practical experiments, the present least-squares treatment does not seem to be different from that of the Cohen's method.

Next, we explain the practical meaning of eq. (14) in detail. For that purpose, we apply eq. (14) to $N$ diffraction lines and have the following equation:

$$S = (4a^2/\lambda^2)^2 \sum_i w_i v_i^2,$$

(15)

This equation can be deduced by referring to the combination $i$ and $j$. Consequently, $S$ is expressed in terms of $v_i$ as follows,

$$S = (4a^2/\lambda^2)^2 \sum_i w_i v_i^2,$$

(16)

where the weighting factor $w_i$ is defined by

$$w_i = \sum_k \sin^4 \theta_k \quad (k \neq i).$$

(17)

When a diffraction line has the highest angular position $\theta_N$ and other lines have smaller angles than $\theta_N$, eq. (17) will be acceptable, because the weighting factors become slightly larger with increasing Bragg angle. This point is quite different from the weighting factor, $w = \cosec^2 2\theta$, proposed by Hess$^{(3)}$. In practice, the present weighting factors are nearly equal to unity, provided that all diffraction lines observed at higher diffraction angles are used to determine the lattice parameters. Therefore, it is said that the present scheme for weighting the measurements is rather similar to that by Cohen, in which the weighting factor is usually taken unity for all diffraction lines.

Acknowledgements

One of the authors (T. Kaneko) would like to thank Prof. M. Kureya, Gunma Technical College, for giving him the opportunity to study on this subject.

REFERENCES

(1) M. U. Cohen: Rev. Sci. Instrum. 6 (1935), 68; 7 (1936), 155.
(2) M. U. Cohen: Z. Kristallogr. A94 (1936) 288, 306.
(3) J. B. Hess: Acta. Cryst. 4 (1951), 209.
(4) A. Lutts: Z. Kristallogr. 161 (1982), 195.
(5) A. Lutts: Z. Kristallogr. 159 (1982), 191.
(6) H. M. Otte and A. L. Esquivel: Trans. Metall. Soc. AIME, 233 (1965), 1276.
(7) M. Hayashi: Nippon Kinzoku Gakkai-shi (J. Japan Inst. Metals), 3 (1939), 123 (in Japanese).
(8) W. B. Pearson: A Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press London, (1967), p. 125.

Appendix

Modification of the observation equation

In the case of hexagonal or trigonal crystal, the quadratic form of the Bragg equation can be written as

$$\sin^2 \theta = (\lambda^2/12a^2)(4S_i + 3l_i^2L) + DF(\theta),$$

(18)

where $S_i$ and $L$ are, respectively, defined as

$$S_i = h_i^2 + h_i k_i + k_i^2$$

(19)

and

$$L = a^2/c^2.$$  

(20)

A modified observation equation is deduced by the same procedure as for the orthorhombic case. Thus, the observation equation analogous to eq. (5) is given by

$$4(\sin^2 \theta_i S_i - \sin^2 \theta S_i) + 3(\sin^2 \theta_l^2 - \sin^2 \theta_i l_i^2)L$$

$$+ \{\sin^2 \theta F(\theta) - \sin^2 \theta F(\theta_i)\} A' = 0,$$

(21)

employing the substitution

$$A' = (12a^2/\lambda^2)D.$$  

(22)

Consequently, the most probable values of $L$ and $A'$ can be obtained by applying the least-
squares method, and then the error-free lattice parameters, \(a_0\) and \(c_0\), can be deduced by the same procedure.

When different characteristic wavelengths are employed to measure the angular positions, for example, the line \(i\) with \(K_\alpha\) radiation and the line \(j\) with \(K_\beta\) radiation are used, the observation equation must be modified, because a parameter \(A\) cannot be written by eq. (6). Therefore, eq. (5) is rewritten in an expression containing the wavelengths, \(\lambda_{K\alpha}\) and \(\lambda_{K\beta}\), namely,

\[
(\lambda_{K\alpha}\sin^2\theta_i k_i^2 - \lambda_{K\beta}\sin^2\theta_i k_j^2)H \\
+ (\lambda_{K\alpha}\sin^2\theta_j l_i^2 - \lambda_{K\beta}\sin^2\theta_j l_j^2)L \\
+ \{\lambda_{K\alpha}\sin^2\theta_i F(\theta_i) - \lambda_{K\beta}\sin^2\theta_i F(\theta_j)\} A'' \\
+ \lambda_{K\alpha}\sin^2\theta_i h_i^2 - \lambda_{K\beta}\sin^2\theta_i h_j^2 = 0, 
\]

employing the substitution

\[
A'' = 4a^2D. 
\]

Almost the same procedure as before is followed to obtain the error-free lattice parameters.