

A Simple Method for the Determination of Lattice Parameters from Powder X-ray Diffraction Data

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A simple method which is suitable for determining with reasonable precision the lattice parameters of the crystals with known structure using a 16-bit personal computer and an unsophisticated calculation is described. This procedure is based on the Nelson-Riley extrapolation function and the least-squares analysis. The lattice parameters of tungsten (cubic), indium (tetragonal), alpha quartz (hexagonal), MgSiO_3 (monoclinic) and $\text{Ca}_2(\text{Mg, Fe})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (triclinic), were determined by this method. The resultant precision was found to be comparable to that by the Cohen's method and the lattice parameters agreed with JCPDS data. The advantages of this method are: the availability of peaks in the medium and low angle regions, the small number of peaks needed, the applicability for all the seven crystal systems, the easy discrimination of experimentally wrong peaks and the easy application by scientists, not necessarily crystallographers.

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I. Introduction

The determination of lattice constants is very important in the study of crystal structure, solubility range, phase identification, physical properties and the determination of solvus curves. For cubic crystals, the graphical method is preferred. For noncubic crystals, although values of a and c can be calculated from $hk0$ and $00l$ reflections, there are however very few such lines available, thus the graphical method is seldom used. The Cohen's method⁽¹⁾⁽²⁾, the Lutts' method⁽³⁾⁽⁴⁾ and a method modified by Kaneko *et al.*⁽⁵⁾ were developed for the determination of lattice parameters from powder X-ray diffraction data. In each of these methods, the procedure is different for different crystal systems. For

complex structures such as monoclinic and triclinic structures, there are very few papers available. Although there are computer programs for calculation, a minicomputer such as VAX is always needed; thus it is not very convenient for some laboratories.

The purpose of this article is to describe a simple method of calculating the lattice parameters from powder X-ray diffraction data on a crystal with known structure. It is based on the Nelson-Riley extrapolation function and least-squares analysis. The following considerations are given: To simplify the calculation as a personal computer will do, to use a minimum number of diffraction lines, to apply the same procedure for different crystal systems and to understand the errors by comparison with the standard deviation, with a hope that it is simple and readily applicable for material scientists, ceramists, physicists, metallurgists and chemists, not necessarily of crystallography profession, in a routine crystal analysis to improve the precision, reliability and reproducibility of their lattice parameter data.

In this paper, simple examples are illustrated for the determination of lattice parameters in

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cubic, tetragonal, hexagonal, orthorhombic, monoclinic and triclinic crystal systems. Also, a comparison in precision between the results of this method and other methods was made using the same experimental data. The calculations were done with a 16-bit personal computer using programs written in Lotus worksheets.

II. Principle of the Procedure

In calculation of the lattice parameter, Cohen⁽¹⁾⁽⁶⁾ assumed

$$\Delta d/d = k' \times \cos^2 \theta. \quad (1)$$

Here $\Delta d = (d_{\text{exp}}) - (d_{\text{cal}})$, $\Delta d/d$ is the fractional error in lattice spacing d , k' is a constant, and θ is the Bragg angle. This equation is valid at $\theta > 60$. Taylor and Sinclair⁽⁷⁾ and, independently, Nelson and Riley⁽⁸⁾ have shown a better extrapolation function

$$\Delta d/d = k(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta), \quad (2)$$

$$\text{let } f(\theta) = (\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta), \quad (3)$$

$$\Delta d/d = k \times f(\theta). \quad (4)$$

In eq. (4) k is the slope of Δd against $d \times f(\theta)$, the relation holds accurately down to very low values of θ and not just at high angles⁽⁹⁾. Therefore a straight line can be drawn through a set of experimental points k_n . Using the same d spacings and lattice constants of JCPDS 5-0642, In the result was shown in Fig. 1. The slope of the line and the deviation of the points correspond to the system and the random errors, respectively, assuming $\theta \neq 90^\circ$, $\cos^2 \theta \neq 0$,

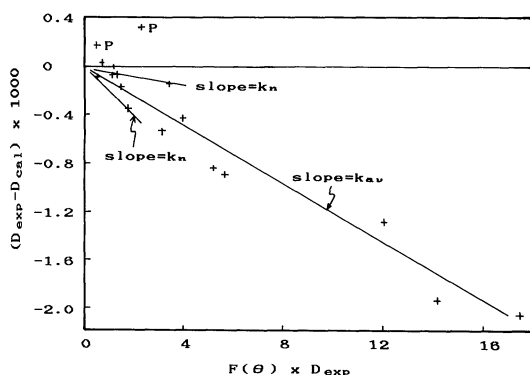


Fig. 1 The plots of Δd against $d \times f(\theta)$.

then

$$\Delta d / (d \times f(\theta)) = k.$$

If there are n diffraction peaks,

$$\Delta d_n / (d_n \times f(\theta_n)) = k_n,$$

and

$$\Sigma \Delta d_n / (d_n \times f(\theta_n)) = \Sigma k_n, \quad (5)$$

$1 / (d_n \times f(\theta_n))$ can be considered as a weighting factor. Usually the system error can be minimized by incorporating an internal standard into sample powder, when

$$k_{\text{av}} = \text{Avg}(k_1 + k_2 + \dots + k_n).$$

There are two ways to find the standard deviation:

$$\text{STD} = \{[(k_1 - k_{\text{av}})^2 + (k_2 - k_{\text{av}})^2 + \dots + (k_n - k_{\text{av}})^2] / (n - 1)\}^{0.5}. \quad (6)$$

Since a systematic error is always of the same sign, an absolute values of k are used to minimize the effect of random errors, thus, a new standard deviation, STD' can be defined as:

$$\text{STD}' = \{[(E_1 - E_{\text{av}})^2 + (E_2 - E_{\text{av}})^2 + \dots + (E_n - E_{\text{av}})^2] / (n - 1)\}^{0.5}, \quad (7)$$

where $E_1 = |k_1|$, $E_2 = |k_2|$, \dots , $E_{\text{av}} = \text{Avg}(E_1, E_2, \dots, E_n)$.

When d_{exp} , H , K and L are known, a set of lattice parameters can be found to minimize the STD' value. Then the set of lattice parameters is the most probable values of the

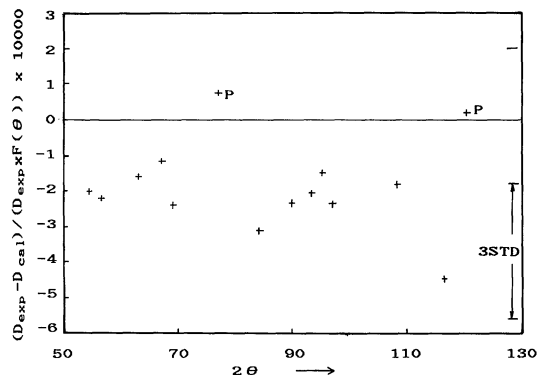


Fig. 2 Using STD' analysis, the plots of $\Delta d / (d \times f(\theta))$ against 2θ .

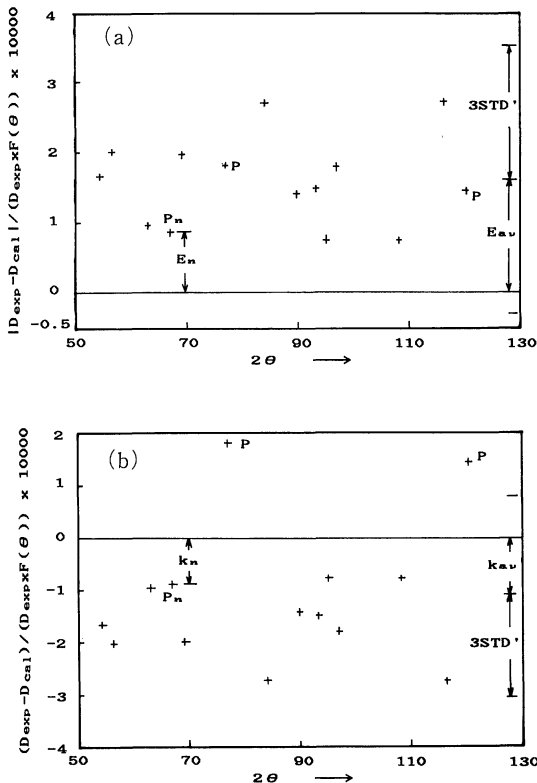


Fig. 3 Using STD' analysis, comparison between (a) as obtained from the absolute values and (b) as obtained from the real values of k_n against 2θ .

crystal's true lattice constants.

The variation in standard deviations are summarized graphically in Fig. 2 (STD) and Fig. 3 (STD'). Figure 2 shows the results of eq. (6). The k_{av} value tends to shift downward due to the balancing effect of positive k 's. Because generally we cannot know any true lattice con-

stant beforehand and we cannot give up any greatly deviated d value, eg., point P in Fig. 2. The STD' is used to minimize random error. The result of eq. (7) was shown in Fig. 3. In (a) as obtained from the absolute values and (b) as obtained from the real values of k were shown, k_{av} and STD' corresponding to the systematic and random errors, respectively. If the difference between k_n and k_{av} is larger than three times of STD', it means that the diffraction angle has an unusual random error and should be double checked. For the sake of increasing the accuracy, the larger Bragg angles were selected in our illustrative works, except where specified as "low angle" calculations. From a number of sets of diffraction lines, the deviations in the lattice constants were worked out.

III. Illustration of the Present Method and Discussion

The authors have taken as the first example the case of α -quartz. Table 1 shows the error between d_{exp} and d_{cal} from the α -quartz crystal, using the same experimental data reported by Lutts⁽³⁾. Here STD' is 4.62 (eq. (7)). Most of the d_{exp} values are smaller than d_{cal} , probably due to the absorption of diffracted beam by the crystal and the Bragg angles are slightly shifted higher.

Table 2 shows a comparison of data from the present and other methods for α -quartz. The results by the present method are in excellent agreement with those calculated by the Cohen's, the Lutts' and the Kaneko's

Table 1 Illustration of lattice parameter calculation for an α -quartz (using the same experimental data reported by Lutts [Ref. (3)] by this method.

No.	θ	$d_{exp}[\text{\AA}]$	H	K	L	$d_{cal}[\text{\AA}]$	$k_n \times 10000$	L.P.
1	85.547	0.89719	2	1	5	0.89720	-8.386	$a=0.491362$
2	83.1865	0.90084	0	0	6	0.90085	-4.074	
3	79.7695	0.90893	2	2	4	0.90896	-4.672	$c=0.540512$
4	77.7985	0.91516	4	1	1	0.91518	-3.362	
5	77.547	0.91603	4	0	3	0.91606	-3.613	STD'=4.62
6	68.66	0.96032	3	2	1	0.96069	-15.202	

$$E_{av} = 6.551(0.000003 \text{ nm})$$

$$k_{av} = -6.55(-0.000003 \text{ nm})$$

$$\text{STD}' = 4.62(0.000002 \text{ nm})$$

$$\text{Where } k_n = (d_{exp} - d_{cal}) / (d_{exp} \times f(\theta))$$

analytical methods using the same diffraction lines. Most important of all, the results of the present method are not varied greatly from various sets of lines. That means we can calculate the lattice parameters from only 2 diffraction lines within a limited error.

Table 3 shows the results for a tungsten (JCPDS 4-0806, cubic), an In (JCPDS 5-0642,

tetragonal) and a MgSiO_3 (monoclinic) specimen. The lines 321 and 004 of In were identified to be outside the 3 STD' range. For the most complex structure such as triclinic crystal structure, the lattice parameters can still be calculated likewise and the results are shown in Table 4. The above results show that this method can be applied to all the crystal

Table 2 Lattice parameters of an α -quartz (hexagonal crystal) obtained by the present method and other methods, using the same Lutts [Ref. (3)] data.

Methods		$a(\text{nm})$	$c(\text{nm})$	STD'(in $d[\text{nm}]$)	
Kaneko's method	F1	0.491355	0.540506		
	F2	0.491355	0.540506		
Lutts' method	B-J extrap	0.491358	0.540510		
	N-R extrap	0.491363	0.540512		
Cohen's method		0.491359	0.540510		
Avg.		0.491358	0.540508		
Present method STD'	1-6*	0.491362	0.540512	4.62	0.000003
	1-5	0.491358	0.540510	5.25	0.000004
	1-4	0.491357	0.540510	5.20	0.000004
	1-3	0.491356	0.540511	0.37	0.000000
	1-2	0.491356	0.540511	0.42	0.000000
	Avg.	0.491357	0.540510	3.2	0.000002
3 σ **		0.000007	0.000002		

* representing the number of peaks used for this calculation.

** σ is the standard deviation of lattice parameters.

Table 3 Comparison among lattice parameter values of W(cubic), In(tetragonal), MgSiO_3 (monoclinic) specimens (using the same experimental data reported by Ref. (10)–(12).

Specimen	Line*	$a(\text{nm})$	$b(\text{nm})$	$c(\text{nm})$	β	STD[nm]
W* (cubic)	Avg.	0.316477				0.00001
	3 σ	0.000007				
JCPDS 4-0806		0.316480				
In** (tetragonal)	Avg.	0.32516		0.49452		0.000006
	3 σ	0.00001		0.00004		
JCPDS 5-0642		0.32517		0.49459		
MgSiO_3 *** (monoclinic)	Avg.	0.96061	0.88171	0.51712	108.287	0.000012
	3 σ	0.00015	0.00013	0.00005	0.003	
JCPDS 35-610		0.96061 (10)	0.88185 (8)	0.51710 (5)	108.289 (10)	

* 8 lines between (110) and (321) were used for calculation.

** 14 lines between (112) and (303) were used for calculation, (321) and (004) outside the normal data range.

*** 14 lines between (202) and (302) were used for calculation.

Table 4 Comparison among lattice parameter values obtained by different set of diffraction lines of a $\text{Ca}_2(\text{Mg, Fe})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Triclinic) specimen (using the same experimental data reported by Blanchard [Ref. (13)]).

	Line*	$a(\text{nm})$	$b(\text{nm})$	$c(\text{nm})$	α	β	γ
Present method STD'	1-14	0.57349	0.67866	0.54612	97.26	108.61	107.25
	3-14	0.57349	0.67862	0.54609	97.27	108.61	107.25
	5-14	0.57349	0.67863	0.54608	97.28	108.61	107.25
	7-14	0.57349	0.67865	0.54608	97.26	108.61	107.25
	9-14	0.57348	0.67864	0.54609	97.26	108.61	107.25
	Avg.	0.57349	0.67864	0.54609	97.27	108.61	107.25
	3σ	0.000012	0.000042	0.000044	0.019	0.005	0.002
JCPDS 35-635		0.57351 (7)	0.67867 (6)	0.54617 (7)	97.25 (1)	108.61 (1)	107.27 (1)

* 14 lines between (330) and (050) were used for calculation, the line (330) outside the normal data range.

Table 5 Lattice parameters obtained by the present method and Cohen's method, using the low and high angle data (JCPDS 33-1161 α -quartz).

		$a(\text{nm})$	$c(\text{nm})$	$k_{\text{av}}[\text{nm}]$	STD[nm]
JCPDS 33-1161		0.49133 (2)	0.54053 (4)		
Cohen's method	Low angle*	0.49165	0.54095		
	High angle**	0.49129	0.54048		
	Difference	0.00036	0.00047		
Present method	Low angle*	0.49138	0.54069	-0.00003	0.000036
	High angle**	0.49130	0.54055	-0.000001	0.000006
	Difference	0.00008	0.00014		

* Low angle: 16 lines between (100) and (212) were used for calculation.

** High angle: 16 lines between (114) and (205) were used for calculation.

Table 6 The lattice parameters of a ZnO (NBS 674) powder obtained by the present method, using our own experimental data, and the Si (NBS 640) as an internal standard.

	Line*	$a(\text{nm})$	$c(\text{nm})$	$k_{\text{av}}[\text{nm}]$	STD[nm]
Present method	1-9	0.32496	0.52063	0.000015	0.000005
	3-9	0.32496	0.52062	0.000014	0.000005
	5-9	0.32496	0.52061	0.000015	0.000004
	7-9	0.32496	0.52060	0.000018	0.000003
	8-9	0.32496	0.52060	0.000021	0.000001
	Avg.	0.32496	0.52061	0.000017	0.000004
	3σ	0.00000	0.00004		
NBS 674		0.32498	0.52065		
		0.00001	0.00001		

* 9 lines between (102) and (104) were used for calculation.

systems and the minimum number of diffraction lines needed is equal to the number of unknown lattice parameters. It shows that the present method gives a reasonably accurate calculation results.

Table 5 compares the present and the Cohen's methods, using the same low and high angle data of α -quartz crystal (JCPDS 33-1161⁽¹⁰⁾). It shows that the present method gives much smaller deviations between results from low and high angle data than the Cohen's method does. This is because that eq. (1) is not suitable for use in the low angle region. In a routine X-ray analysis, if in case of being short of high angle diffraction data, lattice parameters are still deducible from low angle diffraction data with a reasonably small error by the present method. This is extremely meaningful for nowadays X-ray diffractometer practice. Using the present method, Table 6 shows the diffraction result of NBS 674 ZnO powder, measured by a diffractometer. Comparing with the standard lattice parameters, the resultant ones have a remarkable accuracy, and the values of k_{av} , are also presented.

IV. Concluding Remarks

The above proposed method makes possible the attainment of lattice parameters from the X-ray powder diffraction data. Using a 16-bit personal computer and simple calculations, lattice parameters of known crystal structure, from a simple cubic to a complex triclinic structure are able to be determined with reasonable precision. The procedure permits identification of the system error and the random error. It also makes possible sorting out those foreign peaks due to extraneous second phases as unavoidably encountered in daily X-ray diffractometry. Using the present method, in addition to the high angle diffraction lines, the low angle ones are also applicable for lattice parameter calculation. However, high angle

diffractions should be favorably considered as compared to low angle diffractions. The minimum number of diffraction lines needed for calculation is the number of "unknown parameters". By the present method, the calculated lattice parameters with comparable precision to those by the Cohen's, the Lutts' and the Kaneko's method can be obtained. This method is very suitable for routine analyses of the variation of lattice parameters of a material subjected to different processings, and readily available for material scientists, metallurgists, ceramists and chemists, not necessary of crystallography profession. However, the present method is by no means to replace the above analytical methods which are more systematic.

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REFERENCES

- (1) M. U. Cohen: Rev. Sci. Instrum., **6** (1935), 68.
- (2) M. U. Cohen: Z. Kristallogr., **A94** (1936), 288.
- (3) A. Lutts: Z. Kristallogr., **159** (1982), 191.
- (4) A. Lutts: Z. Kristallogr., **161** (1982), 195.
- (5) T. Kaneko, S. K. Gong and O. Nittono: Trans. Japan Inst. Metals, **28** (1987), 95.
- (6) M. U. Cohen: Rev. Sci. Instrum., **7** (1935), 155.
- (7) A. Taylor and H. Sinclair, Proc. Phys. Soc. (London), **57** (1945), 126.
- (8) J. B. Nelson and D. P. Riley: Proc. Phys. Soc., (London), **57** (1945), 160.
- (9) B. D. Cullity: *Elements of X-ray Diffraction*, (1965), 330.
- (10) Swanson and Tatge: JC Fel. Reports, NBS (1949).
- (11) Swanson and Tatge: NBS Circular, **3** (1953), 539.
- (12) Nat. Bur. Stand. (U.S.) Monogr., **20** (1984), 69.
- (13) F. Blanchard: Department of Geology, Uni. of Florida, USA., JCPDS Grant-in-Aid Report. (1984).