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7090 Computer Program for Determination of Precision Lattice Constants

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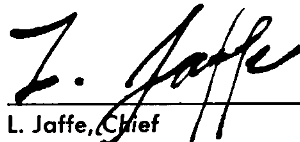

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PASADENA, CALIFORNIA

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ABSTRACT

A 7090 computer program has been developed for the calculation of lattice parameters and their respective accuracies for cubic, tetragonal, and hexagonal materials. The analysis is based on a root-mean-square fit of the data and extrapolation of the lattice constants versus $(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)$. Instructions for use of the program and interpretation of results are included. Comparison of the accuracy of some standard x-ray diffraction techniques is made by means of the program. Results indicate similar accuracy and sensitivity are available with a 114-mm Debye-Scherrer camera, a back-reflection camera, or a goniometer.

I. BACKGROUND

The accurate determination of the lattice constants for various materials is a significant aid in determining their specific atomic makeup. The atomic content of many lattices may vary by means of substitution, by the presence of interstitial ions within the lattice, or by having atoms missing from the lattice. All of these effects normally produce changes in the spacing between the rows of atoms which may be very sensitively detected by means of x-ray diffraction patterns. Of course, additional means of analysis are required to indicate specifically which of the aforementioned processes occurs in any given material but normally the change in lattice parameter is a more sensitive means of determining small variations in lattice spacing.

In addition to this variation in size with composition, the lattice of a material normally expands upon heating. By comparing the lattice parameter at two different temperatures, an accurate calculation of the thermal expansion of a material may be made. Compared with conventional techniques it offers the advantage of high precision and extremely high sensitivity.

II. METHOD OF CALCULATION

The lattice constants for a material are normally calculated from the interplanar spacing (d_{hkl}) and from the appropriate Miller indices. Because most of the errors which exist in the determination of the values of θ and their subsequent d_{hkl} are reduced as the angle of diffraction approaches 90 deg, the more accurate values of the interplanar spacing are obtained in this region. An excellent analysis of the magnitude and dependence of these errors is available in standard x-ray textbooks (Ref. 1). Many techniques are available for the systematic reduction of these errors in the calculation of lattice parameters. These include (1) averaging an arbitrary number of high angle lines, (2) graphically extrapolating the calculated values of d_{hkl} versus various functions of the angle θ to $\theta = 90$ deg, and (3) least-squares techniques involving an analytical extrapolation of d_{hkl} to $\theta = 90$ deg. The third technique, least-squares analysis, offers the advantage of being very precise and highly reproducible; however, by conventional techniques, it is extremely time consuming. With the use of a computer, this disadvantage may be eliminated while retaining all of the advantages.

The program developed here is based on Cohen's least-squares method (Ref. 2) modified to include the function of θ as developed by Nelson and Riley (Ref. 3). It offers the advantages of yielding precise reproducible results for determinations based on a very wide range of θ including all angles above $2\theta = 30$ deg. The program has been developed to be applicable to cubic, tetragonal or hexagonal classes. These three classes encompass almost all high temperature materials, which normally exhibit these simple structures. It was felt that the added complexity introduced by evaluation of the other crystal classes would not be profitable.

The mathematical equations of this program for cubic materials are listed below. The original analysis was conducted by Cohen (Ref. 2) and is available in his original work or in *X-ray Diffraction Procedures* (Ref. 1), p. 467.

If

a_o, c_o = unit cell dimensions

n = total number of points

$$\alpha_i = h_i^2 + k_i^2 + l_i^2$$

$$\delta_i = \sin^2 2\theta \left(\frac{1}{\sin\theta} + \frac{1}{\theta} \right)$$

λ_k = appropriate wavelength of x-radiation

$$A = \frac{\lambda_1^2}{4a_o}$$

D = drift (slope of extrapolation)

θ_i = Bragg angle

KI_i = assigned weight factor

$W_i = KI_i (\tan^2 \theta_i)$

h_i, k_i, l_i = Miller indices

eq. = equivalent

when $\lambda_k \neq 1$, then $\theta_{1\,eq.} = \sin^{-1}[(\lambda_1/\lambda_k)\sin\theta_k]$; $\theta_{1\,eq.}$ is an equivalent value of θ calculated to $k = 1$; $\theta_{1\,eq.}$ is used in computation.

If we let

$$SA = \sum_{i=1}^{n} \alpha_i^2 W_i$$

$$SC = \sum_{i=1}^{n} \alpha_i \delta_i W_i$$

$$SD = \sum_{i=1}^{n} \alpha_i W_i \sin^2\theta_i$$

$$SH = \sum_{i=1}^{n} \delta_i^2 W_i$$

$$SI = \sum_{i=1}^{n} \delta_i W_i \sin^2\theta_i$$

then

$$A = \frac{SD \cdot SH - SC \cdot SI}{SA \cdot SH - (SC)^2}$$

$$D = \frac{SA \cdot SI - SC \cdot SD}{(SC)^2 - SA \cdot SH}$$

The printed out results will show:

LAMBDA = x.xxxxx

A = x.xxxxx AZERO = x.xxxxx D = x.xxxxx

H K L THETA KI DEL F(THETA) DI

SIGMA = x.xxxxxX-xx

where λ, A, D, h, k, l, and KI are defined above and

AZERO = a_o

THETA = $\theta_{i\,eq.}$

$$DEL = A\alpha_i - D\delta_i - \sin^2\theta_i$$

$$F(THETA) = \frac{\cos^2\theta_i}{\sin\theta_i} + \frac{\cos^2\theta_i}{\theta_i}$$

$$DI = \frac{a_o}{\sqrt{h_i^2 + k_i^2 + l_i^2}}$$

$$SIGMA = \sqrt{\frac{\sum_{i=1}^{n} (DEL_i)^2 W_i}{\sum_{i=1}^{n} (n-1) W_i}}$$

For the tetragonal and hexagonal cases the following changes and additions are to be made:

M = 1 for tetragonal case, 4/3 for hexagonal case

$$\alpha_i = M(h_i^2 + h_i k_i + k_i^2) \quad \begin{cases} h_i k_i = 0 \text{ if } M = 1 \\ h_i k_i \neq 0 \text{ if } M = 4/3 \end{cases}$$

$$\beta_i = l_i^2$$

$$A = \frac{\lambda_1^2}{4a_o}$$

$$B = \frac{\lambda_1^2}{4c_o}$$

$$SB = \sum_{i=1}^{n} \alpha_i \beta_i W_i$$

$$SE = \sum_{i=1}^{n} \beta_i^2 W_i$$

$$SF = \sum_{i=1}^{n} \beta_i \delta_i W_i$$

$$SG = \sum_{i=1}^{n} \beta_i W_i \sin^2 \theta_i$$

$$D = \frac{[SG \cdot SC - SB \cdot SI]\,[(SB)^2 - SA \cdot SE] - [SE \cdot SC - SB \cdot SF]\,[SB \cdot SD - SA \cdot SG]}{[SF \cdot SC - SB \cdot SH]\,[(SB)^2 - SA \cdot SE] - [SE \cdot SC - SB \cdot SF]\,[SB \cdot SC - SA \cdot SF]}$$

$$B = \frac{[SG \cdot SC - SB \cdot SI]\,[SB \cdot SC - SA \cdot SF] - [SF \cdot SC - SB \cdot SH]\,[SB \cdot SD - SA \cdot SG]}{[SE \cdot SC - SB \cdot SF]\,[SB \cdot SC - SA \cdot SF] - [SF \cdot SC - SH \cdot SB]\,[(SB)^2 - SA \cdot SE]}$$

$$A = \frac{[SG \cdot SH - SF \cdot SI]\,[SB \cdot SF - SC \cdot SE] - [SD \cdot SF - SC \cdot SG]\,[SE \cdot SH - (SF)^2]}{[SB \cdot SH - SC \cdot SF]\,[SB \cdot SF - SC \cdot SE] - [SA \cdot SF - SB \cdot SC]\,[SE \cdot SH - (SF)^2]}$$

The printed out results will show:

LAMBDA = x.xxxxx M = x.xxxxx

A = x.xxxxx B = x.xxxxx

AZERO = x.xxxxx CZERO = x.xxxxx D = x.xxxxx

H K L THETA KI DEL F(THETA) DI

SIGMA = x.xxxxxX-xx

All of these terms have been defined previously except:

CZERO = c_o

III. APPLICATION OF PROGRAM

The utilization of such a program is independent of the technique used to determine the original data. Because of the need for varied types of sample (powder, solid pieces) it was felt advisable to attempt to determine whether any specific technique of x-ray diffraction as normally practiced offered higher precision than the others. Towards this end, hot-pressed samples of 99.6% pure magnesium oxide and 99.9+% pure aluminum oxide were evaluated by various x-ray diffraction techniques. These included conventional 114-mm Debye–Scherrer camera, x-ray goniometer, and back reflection camera. The results of this comparison of diffraction techniques are shown in Table 1. Unfortunately, none of these methods as available for these investigations contain provision for precision temperature control of the specimen. Thus, it is necessary to rely on room conditioning for control of temperature. For aluminum oxide and magnesium oxide the thermal expansion is relatively low, reducing the magnitude of possible error. However, the maximum variations have been taken, calculated, and are indicated in Table 1.

In all cases standard x-ray diffraction techniques were used. Films were measured using a manual film reader to 0.01 mm. Angles of maximum intensity were determined on the goniometer by scanning the peak at a speed of 0.2 deg 2θ per min. For comparison purposes the National Bureau of Standards values of the lattice parameters are given.

Table 1. Lattice parameter, (Å) of MgO and Al_2O_3 at 26 ±3°C

Material	Technique			a_0	σ_{a_0} [b]	Maximum lattice parameter variation due to temperature	c_0	σ_{c_0} [b]	Maximum lattice parameter variation due to temperature
		Specimen dia., mm	μ_r [a]						
MgO	Debye–Scherrer, 114-mm	1.5	4.4	4.21051	0.00025	0.00024	—	—	—
		0.5	1.55	4.21144	0.00034	0.00024	—	—	—
		0.2	0.62	4.21166	0.00029	0.00024	—	—	—
	Spectrometer	—	—	4.21179	0.00008	0.00024	—	—	—
	Back reflection	—	—	4.21179	0.00008	0.00024	—	—	—
	N.B.S. standard (Ref. 4)	—	—	4.213	—	0.00024	—	—	—
Al_2O_3	Debye–Scherrer, 114-mm	1.5	4.8	4.75867	0.00080	0.00015	13.00764	0.0065	0.00020
		0.5	1.73	4.75822	0.00016	0.00015	12.99799	0.0013	0.00020
		0.2	0.69	4.75872	0.00019	0.00015	12.99818	0.0015	0.00020
	Spectrometer	—	—	4.75837	0.00011	0.00015	12.99840	0.0009	0.00020
	Back reflection	—	—	4.75824	0.00013	0.00015	12.99541	0.0011	0.00020
	N.B.S. standard	—	—	4.758	—	0.00015	12.991	—	0.00020

[a] μ_r = product of specimen radius (mm) and mass absorption coefficient (mm^{-1}).
[b] Calculated according to Appendix.

IV. DISCUSSION OF RESULTS

As may be seen from Table 1 the various x-ray diffraction techniques that were used gave equivalent results both as to value and to standard deviation except where an excessively thick specimen was used. It should be noted that these results are not proposed to be of the highest order of accuracy in that this study was not designed to be a fundamental evaluation of x-ray diffraction techniques. However, it should be noted that with reasonable care in alignment, the diffraction goniometer was capable of yielding results equivalent to film techniques. This, of course, is quite helpful in cases where it is desirable to obtain data from a solid piece without resorting to its destruction to obtain a powder.

APPENDIX

Instructions for Use of the Program

A standard x-ray diffraction pattern should be obtained by any of the conventional techniques. The values of θ obtained should be indexed as to appropriate Miller indices, wave length of x-radiation producing the reflection should be noted, and weight factor should be assigned. The value of the weight factor should be reduced in the case of lines which are broad, diffuse, of exceptionally low intensity, or for any other reason for which the angle may not be accurately determined.

The information should then be submitted to the Digital Computing Analysis and Programming Group on precision lattice parameters determination forms (JPL 0759), a sample of which is shown in Fig. A-1. The following information should be on the form in the areas indicated by the numbers in Fig. A-1:

1. *Specimen identification card.* This is limited to 30 characters including spaces.
2. *Number of points.* This is the total number of values of θ for the particular specimen, including any continuing sheets. Index to the right and do not include a decimal point.
3. *Key.* This number should be zero for cubic material and one for hexagonal or tetragonal material. Index to the right and do not include a decimal point.
4. *M factor.* This space should be blank for a cubic material, 1.00000 for a tetragonal material, and 1.33333 for a hexagonal material. Adjust to the left and include a decimal point counting it as a space.
5. *Number of* λ*'s.* This should contain the total number of λ's used for the determination of the θ's. This is to include the composite $K\alpha_1 K\alpha_2$ value normally used as representing the determining wave length for low angle reflections. Adjust to the right and do not use a decimal point.
6. λ_1, λ_2, λ_3, λ_4. These shall be the most accurate values available for the wave length of the radiation. λ_1 must be $K\alpha_1$. The location of the others is not significant. Adjust to the left and use a decimal point, counting it as a space.
7. *h, k, l.* Place the appropriate Miller indices, *h, k, l,* in 7a, b and c. Adjust each to the left and use a decimal point.
8. θ. This shall be in space 8 to the number of places available. Adjust to the left and use a decimal point counting it as a space.
9. *ki.* The assigned weight factor should be placed in space 9. Adjust to the left and use a decimal point.

PRECISION LATTICE PARAMETER DETERMINATION

PAGE________ OF________

DATE______________

SPECIMEN IDENTIFICATION CARD

1 ① 30

CONTROL CARD

1 NO. PTS. 5	6 KEY* 10	11 M FACTOR 22	23 NO. λ 27
②	③	④	⑤

*0 = CUBIC, 1 = HEX

LAMBDA CARD

1 λ_1 12	13 λ_2 24	25 λ_3 36	37 λ_4 48
(6a)	(6b)	(6c)	

DATA CARDS

1 h 12	13 k 24	25 l 36	37 θ 48	49 ki 60	61 j 65
(7a)	(7b)	(7c)	⑧	⑨	⑩

JPL 0759 DEC 62

Fig. A-1. Standard form for computation of lattice parameter

10. *j*. Space 10 shall be the appropriate subscript of λ for that particular reflection. The particular subscript shall be taken from the location of λ in space 6. For low angle reflections where $\alpha_1\alpha_2$ separation is not achieved, a weighted average wave length should be used.

The form of the printed out data along with appropriate definitions is given in Section II. After computation of results has been completed, the column headed DEL should be examined for single values of an unusually large magnitude. The data for this line should be reexamined for possible errors and the data resubmitted if an error is found.

If the standard deviation for the lattice parameter is desired, it must be calculated from the printed out sigma which is the standard deviation for the angle θ. The calculation is as follows:

$$\sigma^2_{a_o} = \left(\frac{\partial U}{\partial X}\right)^2 \sigma^2_\theta$$

where σ is standard deviation (Ref. 5) and $a_o = f(\theta)$. In this case,

$$A\alpha + B\beta + D\delta - \sin^2\theta = 0;\ \text{assume} \begin{cases} D \approx 0 \\ \alpha, \beta \text{ are constant} \\ A, B \text{ are independent} \end{cases}$$

and

$$A = \frac{\lambda_1^2}{4a_o};$$

differentiating and substituting yields:

$$\sigma_{a_o} = -\frac{\lambda_1}{4\alpha}\frac{\sin^2\theta}{A^{3/2}}\sigma_\theta; \quad \sigma_{a_o} = k_a \sigma_\theta$$

By parallel analysis:

$$\sigma_{c_o} = -\frac{\lambda_1}{4\beta}\frac{\sin^2\theta}{B^{3/2}}\sigma_\theta; \quad \sigma_{c_o} = k_c \sigma_\theta$$

For any given material, k_a and k_c are calculated from the appropriate values of λ_1, A, B, α, β, and θ. It is sufficient to approximate a single value α, β, and θ from the range of data for the specific material, taking into account the weight factor. For many materials k_a is approximately 2.5–3.0.

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4. Swanson, H. E., *et al.*, "Standard X-ray Diffraction Powder Patterns," National Bureau of Standards Circular 539, parts 1 and 9.
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Recipients of Jet Propulsion Laboratory
Technical Memorandum No. 33-109

October 30, 1963

SUBJECT: Errata for Technical Memorandum No. 33-109

Gentlemen:

It is requested that the following changes be made in your copy of Jet Propulsion Laboratory Technical Memorandum No. 33-109, entitled "7090 Computer Program for Determination of Precision Lattice Constants," by M. H. Leipold and W. R. Pauly, dated February 15, 1963:

1. On page 2, second column, change the first equation to read

$$A = \frac{\lambda_1^2}{4a_o^2} \quad \text{instead of} \quad A = \frac{\lambda_1^2}{4a_o}$$

2. On page 3, first column, change the sixth equation to read

$$A = \frac{\lambda_1^2}{4a_o^2} \quad \text{instead of} \quad A = \frac{\lambda_1^2}{4a_o}$$

3. On page 3, second column, change the first equation to read

$$B = \frac{\lambda_1^2}{4c_o^2} \quad \text{instead of} \quad B = \frac{\lambda_1^2}{4c_o}$$

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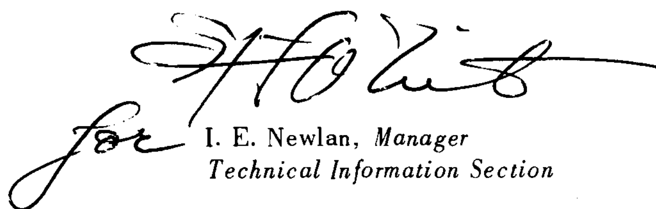
4. On page 7, second column, change the second equation to read

$$A = \frac{\lambda_1^2}{4a_o^2} \qquad \text{instead of} \qquad A = \frac{\lambda_1^2}{4a_o}$$

Very truly yours,

JET PROPULSION LABORATORY



for I. E. Newlan, *Manager*
Technical Information Section