

forming a three-dimensional electron-density synthesis on a general plane affords a ready and graphic means of surveying the crystal structure of a planar molecule to the fullest extent permitted by the measured structure factors.

It is a pleasure to thank Dr Ronald Sass, one of whose programs first demonstrated to us the advantages of the stored table method in computing Fourier series, and Mr J. G. Sime for his part in the earlier three-dimensional structure analysis.

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## A Direct Graphical Method for the Precise Determination of Lattice Parameters of Tetragonal or Hexagonal Crystals

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A direct graphical method for the precise determination of lattice parameters of tetragonal or hexagonal crystals is described. The method is applied to a binary equiatomic Ti-Al alloy and the results presented.

### Introduction

Methods for the precise determination of lattice parameters of tetragonal or hexagonal crystals involve dealing with three unknowns,  $a$ ,  $c$ , and the drift or systematic error. This may be done analytically, as in the Cohen's least-squares method (Klug & Alexander, 1954, p. 485), or graphically by the method of Taylor & Floyd (1950) or the method of successive approximations (Klug & Alexander, 1954, p. 481).

The least-squares solution involving three unknowns is likely to be very tedious and cumbersome, and will yield erroneous results if the diffraction pattern is not perfectly indexed, which is sometimes difficult to do unambiguously in the complex back reflection region. The least-squares method offers no means of checking the validity of input data until after the solution is completed. In addition, this method applies equal emphasis on strong, easily measured reflections and on weak, poorly defined ones.

The graphical method of successive approximations requires a separation of the data into two sets for extrapolation to approximate values of  $a$  and  $c$  separately. The approximate  $c/a$  ratio is used to repeat the extrapolation and obtain more refined values for  $a$ ,  $c$ , and  $c/a$ , and the procedure is repeated as many times as necessary for a stable solution. The method of Taylor & Floyd (1950) uses  $hk0$  reflections to

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determine  $a$  and the slope of the drift line by extrapolation. Then, from a prior estimation of the  $c/a$  ratio, an extrapolation for  $c$  may be made even if only a single  $00l$  reflection is available by using the drift slope from the  $a$  determination, multiplied by the  $c/a$  ratio.

### The direct graphical method

In the course of an investigation on the effects of ternary additions on the lattice parameters of the tetragonal TiAl gamma phase, a direct graphical extrapolation method for tetragonal crystals has been developed. This method can be used as readily for hexagonal crystals, as will be shown later.

The direct graphical method depends upon finding the line of best fit (the drift curve) for a series of straight lines in three dimensional space, each straight line being derived from a particular crystal lattice reflection. Each reflection must, of course, be indexed in order to plot the straight line, which represents the locus of all possible  $a$  and  $c$  values that can account for the reflection, but an advantage of the method is that it shows immediately, by comparison with the other data, when any errors have been made and aids in the correct indexing. While interpretation of the method is based upon a three dimensional concept, its application requires only two dimensions, in effect, a two dimensional projection of the three dimensional situation.

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Table 1. *Diffraction data and calculations for plotting equation of line*

Line	Plane	$\theta$	$4 \sin^2 \theta / \lambda^2 l^2$	$(h^2 + k^2) / l^2$	Equation of line
1	202	32.76	0.1233	1	$(a/c)^2 = 0.1233a^2 - 1$
2	220	33.12	—	—	$a^2 = 15.9020$ (vertical line)
3	113	39.07	0.0744	2/9	$(a/c)^2 = 0.0744a^2 - 0.2222$
4	131	39.73	0.6884	10	$(a/c)^2 = 0.6884a^2 - 10$
5	222	41.62	0.1859	2	$(a/c)^2 = 0.1859a^2 - 2$
8	313	56.40	0.1299	10/9	$(a/c)^2 = 0.1299a^2 - 1.1111$
12	422	70.26	0.3733	5	$(a/c)^2 = 0.3733a^2 - 5$

The equations of the straight lines are based upon a manipulation of the quadratic form of the Bragg equation for tetragonal crystals into the following forms:

$$(a/c)^2 = [4 \sin^2 \theta / (\lambda^2 l^2)] a^2 - (h^2 + k^2) / l^2 \text{ (general form)}$$

and

$$a^2 = \lambda^2 (h^2 + k^2) / 4 \sin^2 \theta \text{ (for } hk0 \text{ planes).}$$

The above equations are straight lines in variables  $a^2$  and  $(a/c)^2$  and can be plotted accordingly to represent possible  $a$  and  $c$  values accounting for a given reflection at Bragg angle  $\theta$ . Fig. 1 shows such a plot for seven reflections from the diffraction pattern of a binary equiatomic TiAl alloy, using data taken from Table 1.

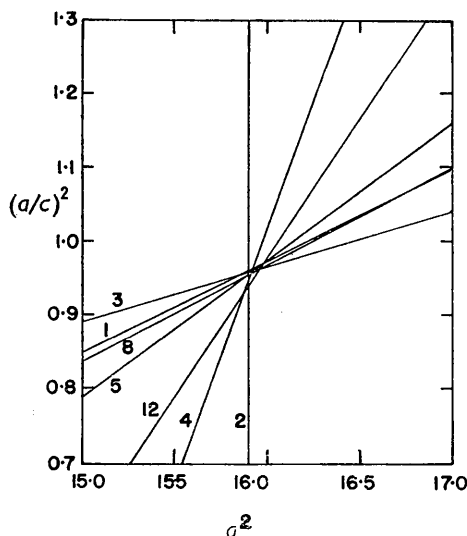


Fig. 1. Diffraction peak lines for TiAl alloy.

It may be seen that the lines fail to intersect at a common point. Ideally, without drift or scatter, such a common intersection would occur. The problem in all practical cases to be solved, by this graphical method as well as the graphical method of successive approximations or the Cohen's least-squares method, is to determine the best solution or line of best fit representing the intersections of the plotted lines. In order to do this it becomes necessary to greatly expand the scale of plotting, as is done for the same

data by Fig. 2(b). At first glance the lines of Fig. 2(b) appear a hopeless jumble, but when it is realized that most of the apparent lack of correlation is due to drift, a semblance of order is noted. The role of drift may clearly be seen by an auxiliary plot, Fig. 2(a), which is derived from Fig. 2(b), and is, in fact, the third dimensional representation previously referred to. It represents graphically the drift factor and is plotted in units of the extrapolation function,

$$\frac{1}{2}[(\cos^2 \theta / \sin \theta) + (\cos^2 \theta / \theta)],$$

to any convenient scale.

The lattice parameter error is a linear function of this extrapolation function over a very wide range of angles, and the lattice parameter extrapolation line will be a straight line when plotted against this function, as in Fig. 2(a). An assumption which is made here is that the drift of  $a^2$  is linear with the extrapolation function, whereas the extrapolation function was derived empirically to be proportional to drift in  $a$ . The substitution of  $a^2$  for  $a$  is justified because of the virtual linearity between  $a$  and  $a^2$  over such a small range as that under consideration—i.e., the parabolic curve relating  $a$  to  $a^2$  is practically a straight line over the interval, say, from  $a^2 = 15.80$  to  $16.00$ . A further assumption is that the  $c/a$  ratio remains constant throughout the range of angular values (the  $c/a$  ratio being unaffected by drift) and that the extrapolation line, when plotted in Fig. 2(b), will be a horizontal line, representing a constant  $(a/c)^2$  value. The problem, then, is to find the horizontal line which is the line of best fit to the diffraction peak lines of Fig. 2(b).

#### The line of best fit

Since it is known that drift is greatest at the lower angles and decreases as  $\theta$  approaches  $90^\circ$ , it is apparent that the line of best fit would have to intersect the diffraction peak lines in a definite sequence, that is, from the lower angle lines to the higher angle lines in regular succession. In this instance, it would cross plotted lines 1, 2, 3, 4, 5, 8, and 12 in that order or the inverse, depending upon whether drift is positive or negative. It is thus a simple matter to place a straight edge horizontally across Fig. 2(b) and adjust it vertically until the lines appear to be intersecting the straight edge in the proper order. In this manner, the area of interest or the range of possible  $(a/c)^2$

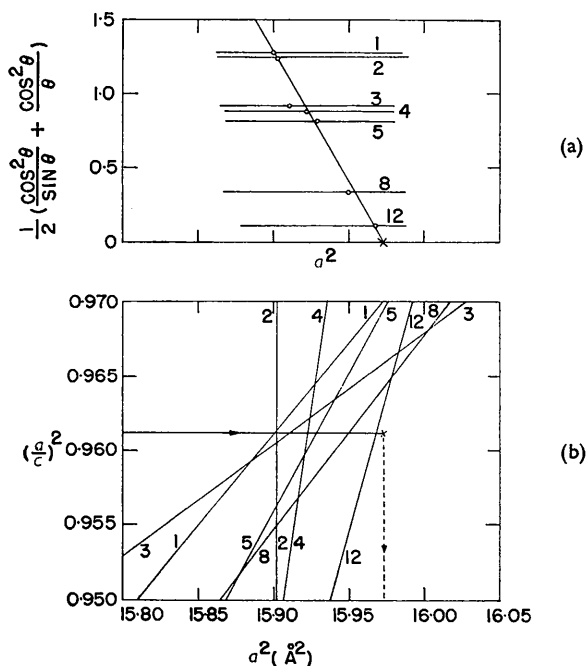


Fig. 2. Graphical extrapolation solution

values can readily be restricted to a relatively small region. The line of best fit can then be found when consideration is taken of the fact that the spacings along the extrapolation line into which it is subdivided by the various diffraction lines will be proportional to the angular values between the diffraction peaks when plotted to the linear extrapolation function.

A simple device for producing a continuously varying scale of the extrapolation function can readily be prepared by plotting all diffraction peak angular values to the scale of the extrapolation function along one ordinate and joining these points, by straight lines, to a common point on the other ordinate. Such a device, shown in Fig. 3, and which is similar to a Bjurström fan diagram (Azaroff & Buerger, 1958, p. 67), is drawn on transparent paper or plastic and superimposed on Fig. 2(b). The transparent fan plotter is moved about on the graph of the diffraction lines until the corresponding lines on the two graphs coincide (intersect) or come in closest proximity along a common horizontal line. This horizontal line gives the  $(\frac{a}{c})^2$  value, and the zero coordinate of this line (corresponding to  $\theta=90^\circ$ ) gives the extrapolated value of  $a^2$ .

The top of the graph, Fig. 2(a), is unessential, but may be used as an aid in portraying the relationship between the drift line and the experimental data. The points of intersection of the drift line (in its horizontal projection) and the diffraction lines are plotted in the upper view against the extrapolation function. The scatter, as well as the drift, in the data is thus graphically shown. If certain of the data are more reliable than others, the scatter from these

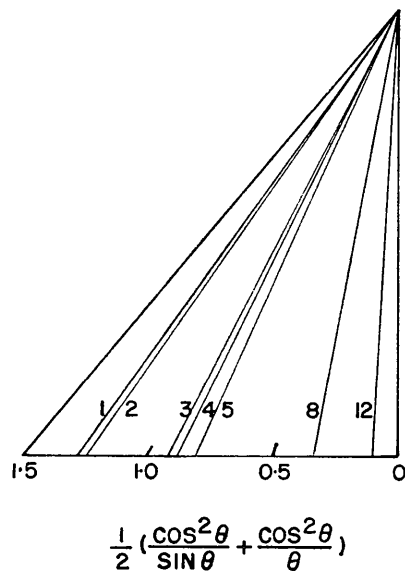


Fig. 3. Extrapolation fan plotter.

points may often be minimized through a judicious adjustment of the horizontal line of best fit.

## Results

The results obtained graphically for the equiatomic Ti-Al alloy are as follows:

$$c=4.077, a=3.997 \text{ \AA}, c/a=1.020.$$

Previous results on an alloy of this same composition are reported by Duwez & Taylor (1952). From graphs of their results, the following are obtained:

$$c=4.063, a=3.997 \text{ kX.}, c/a=1.019.$$

Converting kX. units to  $\text{Å}$  gives:

$$c=4.071, a=4.005 \text{ \AA}.$$

It may be seen that the present results are within 0.2% of those previously reported. The  $c/a$  ratios seem even closer, but it appears that Duwez & Taylor's ratio might be more closely reported as 1.0165, which would make the agreement less good. As a check against some readily available tetragonal substance of well known lattice parameters, a graphical analysis was made of finely powered  $\beta$  tin. The  $a/c$  ratio was found to be 1.832, identical to the published value, and  $a$  was determined as 5.832  $\text{Å}$ , a discrepancy of only 0.001  $\text{Å}$ . (Barrett, 1952, p. 648).

## Conclusion

The above described graphical method of analysis eliminates much of the computational drudgery associated with the least-squares solution, as well as the risk that erroneous data may be introduced, leading

to an incorrect solution. It makes use of the available data in a single step solution, rather than following a procedure of successive approximations or depending upon an assumed value of  $c/a$ .

For hexagonal crystals the direct graphical method may be applied by using the appropriate quadratic forms of the Bragg equation:

$$(a/c)^2 = [4 \sin^2 \theta / (\lambda^2 l^2)] a^2 - 4(h^2 + hk + k^2) / (3l^2)$$

(general form)

and

$$a^2 = \lambda^2 (h^2 + hk + k^2) / 3 \sin^2 \theta \quad (\text{for } hk0 \text{ planes}).$$

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ment Command, for preparation of alloys and Prof. Lars Thomassen, University of Michigan, for a valuable discussion of the method herein described.

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## Short Communications

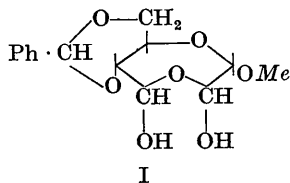
*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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**Crystal data of periodate-oxidised methyl 4,6-O-benzylidene- $\alpha$ -D-glucoside and some of its derivatives.** By J. O. WARWICKER, *The British Cotton Industry Research Association, Shirley Institute, Manchester 20, England*

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Interest in the periodate-oxidation of methyl 4,6-O-benzylidene- $\alpha$ -D-glucoside arises because of the possible analogy with similar reactions occurring in the oxidation of cellulose. The oxidised product I



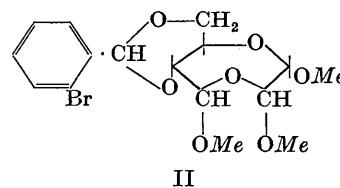
(7,9-dihydroxy-6 $\alpha$ -methoxy-2-phenyl-*trans*-*m*-dioxano[5,4-*e*][1:4]-dioxepan) can be obtained with or without water of hydration by crystallizing from water or from dimethyl sulphoxide respectively (Guthrie & Honeyman, 1959). Needle crystals were obtained from dimethyl sulphoxide. The unit cell dimensions derived from rotation and zero-layer Weissenberg photographs were:

$$a = 24.06, \quad b = 13.18, \quad c = 4.50 \text{ \AA};$$

the space group was  $P2_12_12_1$ . Consideration of the short  $c$ -axis dimension and the space group  $P2_12_12_1$  showed that it was improbable that dimers are formed, and that the correct value of  $Z$  is 4. The measured value of density by flotation was  $1.401 \text{ g.cm.}^{-3}$ . The calculated molecular weight was 301 in good agreement with 298.3, that calculated from the postulated formula I. This provided evidence additional to that of Guthrie & Honeyman (1959) for the correctness of the formula I proposed by them.

Compound I is of interest because it contains a seven-membered ring whose exact conformation and disposition of attached groups are unknown. Some preliminary structural studies to try to elucidate these features were unsuccessful.

An analogue of I, compound II (2-*o*-bromophenyl-6 $\alpha$ ,7,9-trimethoxy-*trans*-*m*-dioxano[5,4-*e*][1:4]-dioxepan) gave needle crystals from ethanol (Colbran, Guthrie & Parsons, 1960).



The unit-cell dimensions were:

$$a = 12.69, \quad b = 30.12, \quad c = 4.43 \text{ \AA};$$

the space group was  $P2_12_12_1$ . The observed density found from a density-gradient column was  $1.582 \text{ g.cm.}^{-3}$ , and for  $Z=4$  the calculated molecular weight was 403.3 in agreement with 405.2 calculated for II.

The conformation of the seven-membered ring and the disposition of the methoxy groups are again unknown. The presence of the bromine atom in this molecule should help in the elucidation of the structure, but no further work is contemplated at the moment.

The phenylhydrazine derivative of I, thought to be III,