structure (1947), one kind corresponding to 5·78 and the other to 2·3 valence electrons.

The writer wishes to express his sincere thanks to Miss Anne Plettinger who took all the diffraction patterns and to Drs J. R. Clark, E. F. Westrum, B. M. Abraham and I. Sheft who provided the silicide samples.

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Limits of Accuracy in the Determination of Lattice Parameters and Stresses by the Debye-Scherrer Method*

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The chief factor in limiting the presently attained accuracy of lattice-parameter determinations and stress evaluations by X-rays is the spectral width of the primary characteristic radiation. At large angles, where the line is most sensitive to changes of lattice dimension, the spectral width predominates over the width due to the geometry of the usual collimating systems. The accuracy of parameter determinations is limited essentially by the accuracy with which the center of such a line can be measured. For a diffraction line with a smooth intensity distribution, recorded on film, the error of measurement caused by the irregular fluctuations of density arising from the film grain is determined experimentally.

It is shown that the present accuracy of stress measurements by X-rays has, in favorable cases, reached the limit given by the spectral width of the characteristic radiation.

1. Theoretical considerations

A. *Introduction*

In past years, the accuracy of lattice-parameter measurements from Debye-Scherrer diagrams has been increased by improvements in technique and calculation methods. The best reported data (Bradley & Jay, 1932; Jette & Foote, 1935) give a relative error of lattice-parameter determination

$$|\delta d/d| \approx 2\times 10^{-5}.$$

Yet, this accuracy is still insufficient for many purposes. It is, therefore, desirable to inquire into the causes which have limited the attainment of higher accuracies.

One source of error is due to the physical nature of the sample; specifically, lattice distortions and small grain size. However, this cause can be removed by adequate preparation of the sample and will not be further discussed; and, for the following discussion, it will be assumed that the sample consists of perfect and identical crystals of sufficiently large size.

A large number of papers have treated the corrections to be applied to the measured line position in order to take into account the absorption by the sample, refractive index, film shrinkage, etc. It will be assumed that all these corrections can be calculated exactly, so that the only remaining source of error is the uncertainty of measurement of the center of a given diffraction line. It is shown later that these assumptions are justified; i.e. that the actual accuracy is as high as can be expected if only the last-mentioned source of error is taken into account.

B. *Line width*

The factor which limits the accuracy with which the center of a diffraction line can be located is its width. It is, therefore, necessary to investigate the causes of line width.

The literature contains a number of extensive discussions of the *geometrical* line width (Lihl, 1932, 1934; Halla & Mark, 1937, p. 159), i.e. that width which is calculated from the geometry of the apparatus and which assumes that the X-ray beam is monochromatic. The width depends on such factors as collimator size, the distance between collimator and specimen, the distance between specimen and film, the thickness of the

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specimen (in the case of transmission), and the absorption in the sample. Fig. 1 shows some representative cases for geometrical widths plotted as a function of the Bragg angle θ.

However, another and very important cause of line width which has received little treatment is that due to the spectral impurity of the primary beam. In order to compare the 'spectral' width with the geometrical width, we shall calculate the form of the diffraction line under the assumption that all geometrical causes of width are negligible.

Let us assume that a randomly distributed mass of perfect crystals is used and that the size of the collimator and the depth of penetration of the beam into the crystal aggregate are negligible. A Debye-Scherrer line would have a width corresponding to the range of wave lengths in the primary beam.

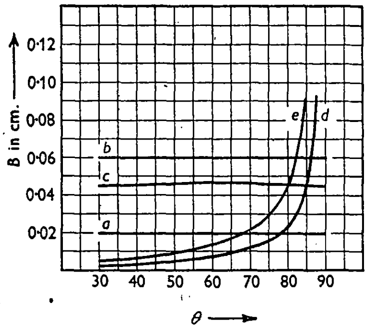

Fig. 1. Line width B as a function of diffraction angle θ. (a) Geometrical width for ideal case in which a focusing condition is used and it is assumed that the diffraction line can be made a faithful image of a collimator of width 0·02 cm. at any Bragg angle. (b) As (a) but with collimator of width 0·06 cm. (c) Geometrical width with sample in form of cylinder of 0·01 cm. diameter, with camera radius of 7·0 cm., and with a circular collimator of width 0·05 cm. placed 8·0 cm. from specimen. This curve is calculated from a formula given by Lihl (1932) for complete absorption. (d) Spectral width calculated from equation (8) for film-to-specimen distance of 5 cm. (e) As (d) but for film-to-specimen distance of 10 cm.

To each wave-length λ, there corresponds on the X-ray photograph an angle $\phi = 2\theta$ given by

$$\lambda = 2d \sin \tfrac{1}{2}\phi, \tag{1}$$

where the order number n is considered to be included in the effective spacing d. The intensity of the incident characteristic radiation, $K\alpha_1$, will be assumed as given by

$$I(\lambda) = \frac{A}{(\lambda - \lambda_0)^2 + (\frac{1}{2}w)^2}, \tag{2}$$

where λ_0 is the wave-length corresponding to the intensity maximum, w is the spectral width* of the line (Fig. 2), and A is a constant.

Let us define an angle $\frac{1}{2}\phi_0$ so that

$$\lambda_0 = 2d \sin \tfrac{1}{2}\phi_0. \tag{3}$$

In substituting (1) and (3) into (2) we obtain for the intensity distribution of the radiation diffracted by all crystals

$$I'(\phi) = \frac{F(\phi)}{(2d)^2(\sin \frac{1}{2}\phi - \sin \frac{1}{2}\phi_0)^2 + (\frac{1}{2}w)^2}, \tag{4}$$

where the function $F(\phi)$ depends on the intensity of the primary beam and may be considered a constant for one given line.

Dividing through by $(2d)^2$ and using (3), we obtain

$$I(\phi) = \frac{C}{(\sin \frac{1}{2}\phi - \sin \frac{1}{2}\phi_0)^2 + (\frac{1}{2}w \sin \frac{1}{2}\phi_0/\lambda_0)^2}. \tag{5}$$

If ϕ is not too close to 180° and the line not too broad, we can make the substitution

$$\sin \tfrac{1}{2}\phi - \sin \tfrac{1}{2}\phi_0 = \Delta(\tfrac{1}{2}\phi) \cos \tfrac{1}{2}\phi_0. \tag{6}$$

Equation (5) thereby becomes

$$I(\phi) = \frac{C}{(\Delta\phi)^2 + (w \tan \frac{1}{2}\phi_0/\lambda_0)^2}. \tag{7}$$

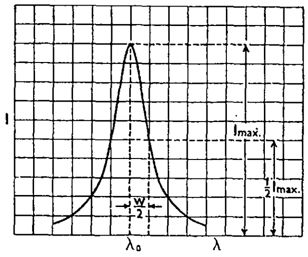

Fig. 2. Spectral intensity distribution for a characteristic X-ray line.

Comparison of (7) with (2) shows that the form of the Debye-Scherrer line is the same as that of the spectral line and that

$$W = 2\frac{w}{\lambda_0} \tan \tfrac{1}{2}\phi_0 \tag{8}$$

is the angular width of the Debye-Scherrer line. Equation (8) expresses the well-known fact that the dispersion increases proportionally with $\tan \theta$. Furthermore, according to (5), the diffraction line is asymmetrical.

Curves (d) and (e) of Fig. 1 represent spectral widths, calculated from (8) for 5 and 10 cm. film-to-specimen distances, respectively. It may be noted that, with conventional collimator sizes, the geometrical width predominates at the lower Bragg angles whereas at very large Bragg angles, 80° or more, the spectral width predominates.

C. *Errors of parameter measurement*

The accuracy with which the center of a line can be located depends on many factors. If a Geiger-Müller counter or ionization chamber is used for recording a line with a smooth intensity distribution, the limit of

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* w characterizes the wave-length spread of the incident characteristic radiation, whereas in the following, 'spectral width' will mean that part of the width of the diffraction line which is due only to the spectral impurity of the characteristic radiation.

accuracy will depend on the stability and sensitivity of the instruments and, in the case of counters, on the counting time. In photographic recording, an otherwise uniform line will appear to have an erratic intensity distribution because of the density fluctuations produced by the film grain. Even with a smooth intensity distribution ideally recorded on infinitely fine-grained film, a limit of accuracy for visual line-center determination is reached because the eye is unable to distinguish density gradations beyond a given value (dependent on the particular observer, density value, type of illumination, etc.).

Let x be the position of the center of a diffraction line of linear width B on a photographic film. The determination of x will be possible only within a finite error δx. Let

$$r = \delta x / B \tag{9}$$

be the relative error of the measurement of such a line. We wish now to discuss the influence of this error upon the accuracy of d, and we must distinguish between two errors, one due to geometrical causes and the other to the spectral impurity of the characteristic radiation.

(1) *Geometrical error.* By logarithmic differentiation of (3), we obtain

$$|\delta d/d| = |\delta\theta_0 \cot\theta_0|, \tag{10}$$

where $\frac{1}{2}\phi_0 = \theta_0$.

If the distance between the film and specimen is R, we may write

$$\delta x = 2R\delta\theta_0. \tag{11}$$

Combining (9), (10) and (11), we obtain for the relative error in the lattice spacing

$$\left|\frac{\delta d}{d}\right| = \left|\frac{\cot\theta_0}{2R} rB\right|. \tag{12}$$

(2) *Spectral error.* The linear width of the diffraction line may be written as

$$B = RW, \tag{13}$$

where W, the angular width, is given by (8). Hence,

$$B = \frac{2Rw}{\lambda_0}\tan\theta_0, \tag{14}$$

and, proceeding as above, we obtain for the spectral error

$$\left|\frac{\delta d}{d}\right| = \frac{rw}{\lambda_0}. \tag{15}$$

The following values of w and λ_0 for two representative X-ray lines have been taken from Compton & Allison (1935, p. 745):

	λ_0(X.)	w(X.)	w/λ_0
Cu $K\alpha_1$	1537·4	0·58	$3{\cdot}7 \times 10^{-4}$
Co $K\alpha_2$	1785·3	0·81	$4{\cdot}5 \times 10^{-4}$

Since the order of magnitude of w/λ_0 is the same for most X-ray lines, we may take $w/\lambda_0 \approx 4 \times 10^{-4}$. Hence, equation (15) becomes

$$|\delta d/d| \approx 4 \times 10^{-4} r. \tag{15a}$$

Fig. 3 shows a comparison between equations (12) and (15a). In both cases, r is considered a constant independent of θ and has been given the value 1/15 (see section on experimental work). Curve (a) represents the spectral error calculated from equation (15a). Curves (b) and (c) are calculated from equation (12) under the assumption that optimum focusing is achieved and that B is constant for all Bragg angles. The assumption that B and r are constant makes the curves (b) and (c) somewhat schematic. However, Fig. 3 does indicate that the major error at the low Bragg angles is caused by the geometrical width, whereas at the larger Bragg angles the spectral error may become comparable with the geometrical error, or predominate. At $\theta = 90°$, the geometrical error vanishes, and the remaining error is spectral. Thus, for $\theta = 90°$,

$$|\delta d/d| \approx 3 \times 10^{-5}.$$

This is indeed the accuracy reported in the best precision measurements.

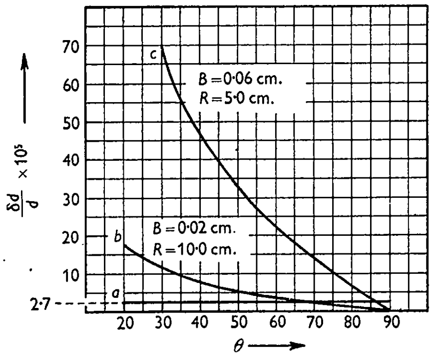

Fig. 3. Relative error of lattice-parameter determination due to inaccuracy of line-center measurement. (a) Spectral error calculated from equation (15a). (b) and (c) Calculated from equation (12), assuming optimum focusing and that B is constant for all Bragg angles.

We conclude that *the present methods for precision lattice-parameter determinations (at high angles of diffraction) reduce all geometrical errors to a negligible quantity. There remains, however, an inherent error of line-center measurement due to an inevitably wide line recorded on film.*

According to curves (a) and (b) of Fig. 3 the relative error in the lattice-parameter measurement at 80° is due practically to the spectral impurity only. Any improvements in the geometry of the apparatus, such as reducing the slit size or increasing the distance between film and specimen, do not lower this error; the only effect is to reduce the intensity of the diffraction line.

D. *Limits of accuracy of stress measurements by the Debye-Scherrer method*

It is well known that the X-ray stress evaluation is based upon a lattice-parameter determination, but that the procedure differs from the method of precision measurement of lattice parameters of unstressed crystals by a number of circumstances unfavorable to the stress method. First, the physical nature of the sample is not a matter of choice. Thus, the crystal grains may be so large that the intensity distribution in the diffraction line becomes exceedingly erratic, or so small that the line becomes wide, and, further, plastic deformation within the sample may give rise to a line of unknown width and intensity distribution. On the other hand, in ordinary lattice-parameter measurements, the crystal size can be chosen to be as favorable as desired. Secondly, a serious source of trouble may arise because of the frequent inability to 'average' a reflection by complete rotation or oscillation of the sample.

A question arises as to whether the present X-ray techniques have overcome these disadvantages of the stress method. Since no direct accuracies of lattice-parameter measurements are reported by those authors who are concerned with stress evaluations, we may calculate the relative error of the parameter determination, $\delta d/d$, from data quoted on the precision of stress determinations.

In a typical case, viz. back-reflection from a steel surface, the sum of the principal stresses, $S_1+S_2=S$, in the surface is given by the relation

$$S=\frac{E}{\nu}\frac{\Delta d}{d},$$

where E is Young's modulus, ν Poisson's ratio, d the lattice value in the unstressed state, and Δd the change in the lattice spacing caused by the stress.

An error in the determination of the lattice change $\delta(\Delta d)$, or, which is the same, $(\surd 2)\,\delta d$ (Worthing & Geffner, 1943, p. 206), gives rise to an error in the stress evaluation by an amount

$$\delta S=\frac{E}{\nu}\frac{\delta d}{d}\surd 2.$$

For steel, we take $E=28\times 10^6$ psi, $\nu=0{\cdot}3$, and, as a reasonable experimentally determined value for the stress error, $\delta S=2000$ psi (Norton & Loring, 1941). Substituting these values into the above expression for δS and solving for the relative error in the spacing, we obtain

$$|\,\delta d/d\,|\approx 2\times 10^{-5}.$$

This is precisely the error of lattice-parameter measurements *per se*, where the nature of the sample and the geometric arrangement are at the observer's choice.

We conclude that the specific disadvantages inherent in the method of stress determinations have, in fact, been substantially overcome and that the actual accuracy is nearly as good as can be expected from errors due only to the limits of accuracy of lattice-parameter measurements in the narrow sense of the word, i.e. under the most favorable conditions chosen. Therefore, the discussion of the previous sections applies also to stress measurements, and it can be concluded that the present limit of accuracy is due to the spectral width of the primary radiation.

2. Experimental work

Given a diffraction line with a smooth intensity distribution, how accurately can the line center be determined from a photographic record? It is apparent that the result will depend on the grain size of the film, the density level of the exposure, and the processing conditions. Consequently, only a few representative cases will be considered here.

We shall consider a subjective and an objective method for the line-center determination, and the standard deviation of measurement, σ, will be determined for both cases.

In a normal distribution of errors, the frequency of errors outside the range $\pm 3\sigma$ is very small; the number of observations beyond this limit will be less than 1 % of the total number of observations. Hence, with the expectation that practically all measurements of the line center will fall within the range $\pm 3\sigma$, the relative uncertainty of line-center measurement becomes

$$r=3\sigma/B.$$

A. *Subjective accuracy*

In this method, four experienced observers visually estimated the center of a diffraction line.

A broad line was produced by irradiating a polycrystalline sample of zinc with Cu $K\alpha$ radiation. The $K\alpha_1$ component gave rise to a 213 reflection at a Bragg angle of 87·5°; the $K\alpha_2$ component did not appear. A narrow line, also used in the subjective measurements, was simply a $K\alpha$ doublet occurring at a small Bragg angle on a Debye-Scherrer diagram. In both cases, the lines were obtained by rotating a cylindrical aggregate of the sample about an axis normal to the incident beam. This guaranteed a perfect crystal statistics which gave a diffraction line exhibiting a smooth intensity distribution.

The measuring instrument was a comparator equipped with crosshairs in the viewing lens, and the illumination and magnification were chosen to be convenient for all observers. Each participant made several measurements of the line center and the data of each observer were averaged. The average value was considered to be the best line-center estimation for the particular observer. The best values of all observers were averaged and the standard deviation was calculated from the latter value. The results are presented in Table 1, where R is the distance between the film and the sample. Obviously, the number of measurements is so small that no exaggerated weight should be attached to these numbers. Furthermore, as we have pointed out, film quality, film density, developing conditions, etc., may change these results. Nevertheless, the increased relative accuracy for broader lines seems to be a fact.

Table 1. *Visual estimation of centres of diffraction lines*

	σ(cm.)	$B=RW$(cm.)	$r=3\sigma/B$
Sharp line	0·00075	0·015	1/7
Broad line	0·00074	0·077	1/35

This is also in agreement with what one would expect theoretically. Indeed, if the line width is of the order of one grain or cluster of grains, the ratio r will be of the order one. If, on the other hand, the line width is very large in comparison with the 'quasi-period' of the fluctuations of density, the uncertainty of the maximum will be relatively small so that r should decrease.

We have observed that the data given by any one observer were far more consistent than the average values of each of the four observers. A plausible explanation is the following.

The cross-hair is placed at that point on the recorded line which shows the highest photographic density. However, a large grain or grain cluster will be considered by the observer to be the point of maximum density, and this cluster will generally serve as a guide to the cross-hair, resulting in a high reproducibility for the particular observer. Another observer will also show high reproducibility of his measurements, using another grain or grain cluster as a reference. Of course, finer-grained film will result in an improved accuracy for the line-center measurement.

The limit of the reproducibility by one observer depends on the width of the cross-hair, the resolution of the microscope and the micrometer screw. Actually, the accuracy as given in Table 1 is about five times lower than the reproducibility; the error is definitely due to the granular nature of the film.

We have indicated that the spectral width becomes comparable with the geometrical width at about 80°. Thus, it would be desirable to determine the measurement of a line center at this angle. However, for the usual film-to-specimen distance of 6 cm., the proximity of the $\alpha_1\alpha_2$ doublet influences the subjective evaluation of one of the lines. Consequently, we can only interpolate the r value at 80° from Table 1. Thus, the 310 reflection of Fe by Co $K\alpha_1$ has an angular width of 0·0054 radians. For a film-to-specimen distance of 6 cm. the line width, RW, would be 0·032 cm. From Table 1 this would yield

$$r = 1/15,$$

which may be taken as a representative figure for the subjective accuracy if all reservations made above are remembered.

B. *Objective accuracy*

The objective studies were performed by determining the median of the microphotometer tracing of a diffraction line.

In a microphotometer tracing, the grain clusters, film defects, scratches, dust, etc., will be recorded and will vitiate the determination of the median, whereas such spurious fluctuations of density on the film will generally be recognized as such and will be disregarded by the eye so that the eye has the advantage of critical discrimination. On the other hand, the eye is less able than the microphotometer to distinguish slight gradations of density. It should be expected, therefore, that the visual measurement would be superior for narrow lines, whereas, for broad lines, the objective determination of the median will be better. Consequently, only broad lines were chosen for the objective measurements.

Diffraction lines of varying widths were recorded on coarse-grained and fine-grained film. The broad lines, as in the case of the subjective studies, were the 213 reflections of polycrystalline zinc, obtained by rotating the sample. On the other hand, a narrower line was produced by exposing a rotating film to a narrow beam of X-rays. This permitted measurements on a sharp line which was not composed of an overlapping $K\alpha$ doublet.

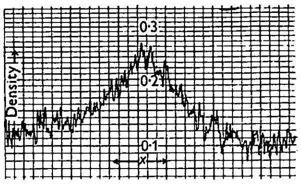

Fig. 4

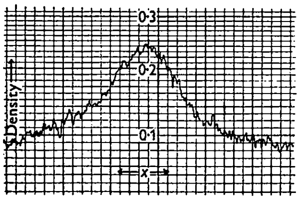

Fig. 5

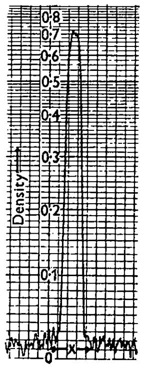

Fig. 6

Fig. 4. Microphotometer tracing of broad line recorded on coarse-grained film.

Fig. 5. Microphotometer tracing of broad line recorded on fine-grained film.

Fig. 6. Microphotometer tracing of a sharp line recorded on coarse-grained film.

The microphotometer beam was 1 mm. long and 0·01 mm. wide, and care was exercised to record grain clusters, film defects, etc., so that no arbitrary averaging of the tracing would occur. This will account for irregularities in the tracing, but to have used a larger beam for averaging would have defeated the purpose of the experiment.

A tracing was produced by scanning along the width of the line. The scanning was repeated in order to obtain a duplicate tracing. The film was then rotated in its own plane so that a new region of the line would be presented to the microphotometer beam. The width of the line was scanned again and, as before, a duplicate tracing was made. Five sets of tracings, or a total of ten, were so obtained for each film. Typical microphotometer records are shown in Figs. 4, 5 and 6.

A sufficient region of the film on either side of the line was recorded in order to establish a base line. The curves were then carefully removed from the record by cutting along the tracing and along the base line for a specified distance on either side of the intensity maximum. The medians were determined by the usual process of cutting the abscissa at some point x. The half-curves so obtained were weighed with a chemical balance and, after several cuttings and weighings, two half-curves with equal weight were obtained. After the balance had been effected, the distance between the cut edge and a fiducial mark on the tracing was measured. This value constituted the X coordinate for the median.

The standard deviation was determined from the X coordinates of a given diffraction line and, as before, $\pm 3\sigma$ was taken as the value beyond which the number of observations having this error would be negligible.

The results are presented in Table 2.

Table 2. *Photometric estimation of centers of diffraction lines*

	σ (cm.)	$B=RW$ (cm.)	$r=3\sigma/B$
Coarse film, sharp line	0·0018	0·034	1/6
Coarse film, broad line	0·0034	0·17	1/18
Fine film, broad line	0·0026	0·18	1/23

The general tendency for increased relative accuracy for wider lines is again apparent. However, it is surprising that, for lines broader than those evaluated visually, the accuracy is lower. It seems that the discriminating ability of the eye makes it superior to the microphotometer for the usual range of line width.

In a more accurate method of objective evaluation, one would first have computed, by the method of least squares, the best-fitting curve corresponding to each microphotometer tracing and then have determined the median. However, this procedure appears too cumbersome for routine use.

It is doubtful whether the present choice of exposure time and background density are the most favorable. Only further investigations can answer the question.

3. Conclusions

The minimum width of a diffraction line depends on the spectral impurity of the incident characteristic radiation. It has been shown that at large diffraction angles, 80° or more, the spectral width will predominate over the geometrical width.

Such a diffraction line, produced with a smooth intensity distribution, will appear irregular when recorded on film because of the fluctuations in density caused by the film grain. The limit of accuracy of lattice-parameter determination is reached because of the error of determination of the intensity maximum of a wide line photographically recorded. Objective and subjective measurements of the error in determination of the line center lead to a relative error $|\delta d/d| \approx 3\times 10^{-5}$, *due to the spectral width alone*, in agreement with the best reported accuracy.

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The Crystal Structure of Groutite, $HMnO_2$

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The crystal structure of groutite, a new modification of $HMnO_2$, has been determined. The dimensions of the orthorhombic unit cell are $a=4{\cdot}58$ A., $b=10{\cdot}76$ A., and $c=2{\cdot}89$ A., and the space group is D_{2h}^{16}–$Pbnm$. The atomic arrangement is very nearly identical with that of diaspore.

Introduction

The crystallography of groutite, which has been reported by Gruner (1947), indicates that it is a member of the diaspore–goethite group. In a preliminary X-ray diffraction study the size of the unit cell was indicated as $a=4{\cdot}56$ A., $b=10{\cdot}70$ A., and $c=2{\cdot}85$ A. or possibly twice the last value. Since manganite does not show the same structure as the isoformular aluminum and iron minerals, boehmite and lepidocrocite, it was thought advisable to make a determination of the unit cell, space group, and structure of groutite in order to make certain of its identification as a member of the diaspore–goethite group.

The unit cell and space group

A crystal with no dimension larger than 0·3 mm. was selected. The Laue symmetry mmm was verified, and the unit-cell values $a=4{\cdot}58$ A., $b=10{\cdot}76$ A., and