A Method of Determining Cubic Lattice Parameters Suited to the Conditions of High- and Low-Temperature Powder Diffractometry

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Abstract

A method of measuring accurate cubic lattice parameters is developed which is suited to the type of conditions encountered in high- and low-temperature powder diffractometry. This is based on the fact that the absolute Bragg angle of each line in an indexed cubic diffraction pattern can be determined from a knowledge of the differences in angles between lines. Accurate zero-angle alignment, therefore, is unnecessary. Furthermore, it is shown that the peak or centroid shift of the line profiles arising from the instrumental and physical aberrations can be determined directly from the measured angular data without assuming a specific angular dependence. In practice the accuracy of the method is of the order of 0.0002 Å for a lattice parameter of approximately 8 Å.

Introduction

Many high- and low-temperature attachments used on X-ray powder diffractometers are not designed for the measurement of accurate lattice parameters. In particular, there is frequently no means of carrying out accurate zero-angle alignment with respect to the incident beam and the specimen surface cannot always be located accurately or reproducably on the diffractometer axis. A commercial low-temperature attachment used in this laboratory, for instance, cannot be operated at 2θ < 30° owing to obstructions in the incident and diffracted beams and so less-precise alignment procedures have to be adopted.

Even with well-designed attachments, problems can arise which would not normally be encountered under standard room-temperature conditions. When the temperature of the specimen and its supports is changed, expansion or sintering can occur and the position of the sample surface may alter relative to the diffractometer axis. In addition, at high temperatures (~1000 K) the peaks of the high-angle diffraction lines tend to be less well defined or non-existent owing to the dominant effect of the temperature factor. In this situation greater emphasis has to be placed on the measured peak positions of lower-angle diffraction lines when determining lattice parameters. The question addressed in this paper, therefore, is how can lattice parameters be measured accurately, given that there are possibly large systematic errors in the measured data which vary not only from specimen to specimen, but also with the temperature of measurement?

Discussion of some limitations of standard methods of lattice-parameter determination

Under normal circumstances an instrument may be calibrated by incorporating an internal standard within the specimen being measured. Unfortunately, at high temperatures this approach is of limited value as standard materials are only well defined under room-temperature conditions. Also, a standard will often react chemically with the specimen under consideration, particularly when the experiment is carried out over a long period of time. Moreover, when integrated intensities as well as line positions are being measured the extra diffraction lines arising from a standard may interfere with the diffraction lines of interest.

Extrapolation techniques (see for instance Klug & Alexander, 1974) are also of limited value under the conditions described and especially when the analysis is based on lower-angle diffraction lines (i.e. 2θ < 130°). To illustrate this consider the following example which is intended to be typical of the situation met with in high- and low-temperature diffractometry. Suppose we assume a specimen with its surface displaced 0.5 mm from the axis of a diffractometer of radius 173 mm when the zero-2θ error is 0.10° 2θ. The total instrumental shift f(θ) of each diffraction line from its true Bragg angle θ for this combination will be given, according to Wilson (1963), by f(θ)=0.050 + 0.166 cos θ (°θ). If we now simulate a diffraction pattern which includes this shift, an extrapolation plot of the measured lattice parameters may be generated with the extrapolation function appropriate for specimen surface displacement (i.e. a vs cos θ cot θ; Wilson, 1963). This is done in Fig. 1 with the expected diffraction lines for a cubic spinel oxide whose correct lattice parameter was chosen to be 8 Å exactly. This graph
illustrates quite clearly that the extrapolation approach is not a reliable method for eliminating the two aberrations because

(i) the graph appears to be linear even though a large zero error is present in the data.
(ii) the extrapolated value for the lattice constant is 8.0025 Å and not 8.0000 Å as expected.

To obtain reliable results by this method it is necessary to use diffraction lines at 2θ angles in excess of 150°.

In the analytic least-squares approach to lattice-parameter measurement (also reviewed in Klug & Alexander, 1974), it is possible to determine the relative magnitudes of the zero shift and specimen displacement contributions in the example quoted by fitting an aberration line-shift \( f(θ) \) to the data of the form

\[ f(θ) = p + q \cos θ. \]

However, when only low-angle lines are available for analysis and when other aberrations as well as noise are evident in the data, accurate interpretation of the results becomes increasingly difficult. This occurs because the mean-square fit to the measured lattice parameters often exhibits a rather broad flat minimum in the vicinity of the optimum values for \( q \) and \( p \). The problem here is analogous to the situation encountered with the extrapolation approach.

The common practice in least-squares analysis of assuming a form for \( f(θ) \) represented by a sum of trigonometrical terms can also lead to errors as this assumption is only valid when centroid angles are employed as the measure of line position. When peak angles are employed, \( f(θ) \) possesses a complex angular dependence which arises because the component instrumental aberration profiles are convoluted together and do not contribute independently to the total peak shift (Wilson, 1963). Any expression chosen to describe \( f(θ) \), therefore, can only represent an algebraically equivalent version of the actual expression over the range of the data. This is probably not a serious problem when employing high-angle lines because the peak shifts arising from the geometrical aberrations are additive and similar in value to centroid shifts to a first-order approximation (Wilson, 1963). However, with many diffraction patterns, such as those from mineralogical specimens (e.g. garnets and spinels), the problem of profile overlap at high angles can preclude the use of high-angle peaks in lattice-parameter measurement. Unless some form of profile-fitting procedure is adopted, therefore, only lower-angle diffraction lines (typically 2θ< 130°) can be used for this purpose which then poses the problem of assigning a valid form for \( f(θ) \).

In this paper an alternative technique for measuring cubic lattice parameters is presented which overcomes some of the above problems. This is done by extending the method developed by Goldak (1961) and Popovic (1971, 1973) who showed that the reference angle from which line-profile angles are measured need not be the mechanical zero of the diffractometer. In fact, the fundamental measurement recorded in their method is the difference in Bragg angle \( φ \) between profiles of known Miller indices. By using this approach the absolute Bragg angle can be determined free of any error arising from misalignment of the 2θ-zero position and without recourse to measurements based on the 4θ value of the diffraction cone (e.g. Bond, 1960; Cernohorsky, 1960; King & Vassamillet, 1962). Despite this, the method has only been exploited to a limited extent (Halliwell, 1972). The intention in the present work, therefore, is to indicate how it may be exploited to realize an accuracy normally obtained by standard methods, but under circumstances which would be considered unfavourable. Perhaps the most unique feature of the method proposed is that the line shift \( f(θ) \) is derived directly from the experimental data without having to predict in advance which instrumental factors dominate its angular dependence.

**Method**

The equations developed by Goldak (1961) for cubic materials express the absolute Bragg angles \( θ_1 \) and \( θ_2 \) of a pair of diffraction lines in terms their angular separation \( φ = θ_2 - θ_1 \), i.e.

\[
\tan θ_1 = \frac{\sin φ}{R - \cos φ}
\]
In general, the derived values \( \phi \) will be nominally the derived values for each particular line. In a pattern comprising \( r \) lines there will be \( r-1 \) derived values for each line. For an indexed diffraction pattern in which the only systematic error present in the data is a zero-20 error, the values for \( \theta_1 \) and \( \theta_2 \) calculated from these equations will be automatically corrected for this error. This aspect of the equations is extremely useful when the geometrical constraints of a diffractometer prevent accurate zero-angle alignment being carried out. When the above equations are applied to an experimental pattern containing additional systematic errors the recommended procedure (Goldak, 1961) is to use pairs of lines which are widely spaced (i.e. \( \varphi \) large). This reduces the influence of measurement errors on the calculated values for \( \theta_1 \) and \( \theta_2 \) from (1a) and (1b).

Conversely, if \( \theta_1 \) and \( \theta_2 \) are derived from a pair of closely spaced lines (e.g. \( K_{\alpha 1} \) and \( K_{\alpha 2} \) for the same \( hkl \) reflection), the values obtained tend to be grossly different from the true values. This marked dependence of the error in the derived \( \theta \) values on the choice of angular separation \( \varphi \) reflects the fact that the accuracy of (1a) and (1b) is extremely sensitive to the angular dependence of the systematic errors in the experimentally measured Bragg angles. It is this property of the equations along with their ability to correct for zero error which is exploited in the present work to evaluate the line shift \( f(\theta) \) of each measured line relative to its true Bragg angle.

In the following analysis various types of diffraction angle are referred to; these are defined as follows:

(i) \( \theta \) represents the Bragg angle of each diffraction line corrected for all systematic errors.

(ii) \( \alpha \) represents the measured angle of a diffraction line (i.e. peak or centroid value). Under standard powder diffractometer conditions \( \alpha \approx \theta \), but under the present scheme this would not necessarily apply, as the zero condition for \( \alpha \) can be significantly different from the condition \( \theta = 0 \). In an example considered later in this paper the condition \( \alpha = 0 \) corresponds to \( \theta \approx 17^\circ \).

(iii) \( \psi \) represents the Bragg angle derived from a pair of diffraction lines (i.e. \( \alpha_i \) and \( \alpha_j \)) with equation (1). The derived value \( \psi_{ij} \) for the \( i \)th line using the \( j \)th line to form the pair will depend on the angular separation \( \varphi_{ij} = \alpha_j - \alpha_i \), i.e.

\[
\tan \psi_{ij} = \frac{\sin \varphi_{ij}}{R - \cos \varphi_{ij}}, \quad i \neq j.
\]

Consequently, for a pattern comprising \( r \) lines there will be \( r-1 \) derived values for each particular line. In general, the derived values \( \psi_{ij} \) will be nominally the same as the Bragg angle \( \theta \), but will require correction for equality to be exact. In the absence of systematic errors each set of angles will be identical. The presence of systematic errors in the data, therefore, will be reflected by the differences between these sets of angles and a variation of \( \psi_{ij} \) for each line (i.e. \( i \) fixed), with angular separation \( \varphi_{ij} \). In this analysis the line shift \( f(\theta) \) arising from the systematic errors is defined in terms of the experimental and corrected Bragg angles as

\[
f(\theta) = \theta + f(\theta).
\]

The actual function observed and exploited here to determine \( f(\theta) \) for each line is the difference \( \delta(\alpha_i, \alpha_j) \) between the derived value \( \psi_{ij} \) and the original experimental angle \( \alpha_i \), i.e.

\[
\delta(\alpha_i, \alpha_j) = \alpha_i - \psi_{ij}.
\]

To relate the observed function \( \delta(\alpha_i, \alpha_j) \) to \( f(\theta) \) we must examine the effect of using the measured angles \( \alpha_i \) and \( \alpha_j \) in (1a) rather than the true Bragg angles \( \theta_i \) and \( \theta_j \). This may be done by employing the definition given by (2),

\[
\tan \theta_i = \frac{\sin(\alpha_j - \alpha_i) - [f(\theta_j) - f(\theta)]}{R - \cos(\alpha_j - \alpha_i) - [f(\theta_j) - f(\theta)]}, \quad (4)
\]

As the difference in the line shifts \( [f(\theta_j) - f(\theta)] \) is small, (4) may be expanded to a first-order approximation giving the difference \( \delta(\alpha_i, \alpha_j) \), i.e.

\[
\delta(\alpha_i, \alpha_j) = \frac{f(\theta_j)\tan \theta_j - f(\theta)\tan \theta_i}{\tan \theta_j - \tan \theta_i}, \quad (5)
\]

where \( \theta_i \) and \( \theta_j \) represent the nominal Bragg angles of the \( i \)th and \( j \)th lines. When \( \alpha \approx \theta \), the nominal Bragg angles \( \theta_i \) and \( \theta_j \) can be replaced by \( \alpha_i \) and \( \alpha_j \). On the other hand, when \( \alpha \) is very different from \( \theta \) the average derived values \( \psi_i \) and \( \psi_j \) for the \( i \)th and \( j \)th lines may be used to represent the nominal Bragg angles.

Equation (5) is the basic equation from which the present analysis is developed. By inspection of this equation it is clear that if zero-20 error is the only systematic error present [i.e. \( f(\theta) = \text{constant} \)] then \( \delta(\alpha_i, \alpha_j) \) is constant and equal to \( f(\theta) \), i.e.

\[
\delta(\alpha_i, \alpha_j) = f(\theta) = \text{constant}.
\]

In general, \( \delta(\alpha_i, \alpha_j) \) for the \( i \)th line will vary with \( \alpha_j \) but not in the same manner as \( f(\theta) \). Nevertheless, this variation can still be employed to determine \( f(\theta) \) and subsequently the true Bragg angle \( \theta \) of each line.

One method of approaching this problem is to extrapolate the variation of \( \delta(\alpha_i, \alpha_j) \) for each line (i.e. \( \alpha_i \) fixed) to the limit \( \theta_j = \pi/2 \). This gives the value \( f(\theta_j) \) directly, i.e.

\[
\lim_{\theta \to \pi/2} \delta(\alpha_i, \alpha_j) = f(\theta_j).
\]
An illustration of this variation is given in Fig. 2 for a set of data obtained from the Kx, peak angles of a cubic diffraction pattern. Unfortunately, this approach is susceptible to misinterpretation in much the same manner as the standard lattice-parameter extrapolation technique referred to earlier. As the data from high-temperature diffractometers is often of the lower-angle type (i.e., $2\theta < 130^\circ$), the use of extrapolation to determine $f(\theta)$ is not discussed further.

To overcome the limitations of extrapolation an intrinsically more accurate procedure based on interpolation has been developed. In this, the difference function $\delta(\alpha_i, \alpha_j)$ for each line (i.e., $\alpha_i$ fixed) is interpolated to $\bar{\theta} = \pi/4$ to give the function $\Delta(\alpha_i)$ defined as

$$\Delta(\alpha_i) = \lim_{\bar{\theta} \to \pi/4} \delta(\alpha_i, \alpha_j).$$

In principle, any angle within the scope of the data may be employed as the interpolation angle. The use of $\pi/4$ is justified by the fact that subsequent equations derived for this condition tend to be easier to manage. The form of the difference function $\Delta(\alpha_i)$ at the chosen condition is given by

$$\Delta(\alpha_i) = \frac{f(\bar{\theta}) - f(\pi/4) \tan \bar{\theta}_i}{1 - \tan \bar{\theta}_i}. \tag{6}$$

When this equation is rearranged an expression for the line shift $f(\bar{\theta})$ can be obtained:

$$f(\bar{\theta}) = \Delta(\alpha_i) (1 - \tan \bar{\theta}_i) + f(\pi/4) \tan \bar{\theta}_i. \tag{7}$$

At this stage the problem of determining $f(\bar{\theta})$ is reduced to the determination of $f(\pi/4)$. Once again, extrapolation may be used to determine $f(\pi/4)$ as

$$\lim_{\bar{\theta}_i \to \pi/2} \Delta(\alpha_i) = f(\pi/4). \tag{8}$$

For data of limited angular range it is essential that any fitting procedure be kept within the scope of the data and as such this approach is not discussed further.

A successive approximation technique has therefore been formulated to find $f(\pi/4)$ through an analysis of $\Delta(\alpha_i)$ in the vicinity of $\bar{\theta}_i = \pi/4$. The value of this function at $\bar{\theta}_i = \pi/4$, $A_0$ say, is given by applying L'Opital's rule to (6):

$$A_0 = f(\pi/4) - f'(\pi/4)$$

or

$$f(\pi/4) = A_0 + f'(\pi/4). \tag{9}$$

The differential term $f'(\pi/4)$ in (9) may be found by carrying out a similar limiting procedure on $d\Delta(\alpha_i)/d\bar{\theta}$ at $\bar{\theta} = \pi/4$, i.e.

$$\lim_{\bar{\theta}_i \to \pi/4} \left\{ \frac{d\Delta(\alpha_i)}{d\bar{\theta}} \right\} = A_1 = f'(\pi/4)/2 - f''(\pi/4)/4 \tag{10a}$$

or

$$f'(\pi/4) = 2A_1 + f''(\pi/4)/2. \tag{10b}$$

By repeating the limiting process with higher derivatives of $\Delta(\alpha_i)$ a series of expressions for $f(\pi/4)$ can be generated, each of which contains a residual differential term of the form $f'(\pi/4)/N$. These are listed below for the limits corresponding to $r = 1$ to $r = 6$:

$$f_0 = A_0 + A_1/2 \tag{11a}$$
$$f_0 = A_0 + A_1 + f_2/4 \tag{11b}$$
$$f_0 = A_0 + 3A_1/4 + 3A_2/8 + f_3/16 \tag{11c}$$
$$f_0 = A_0 + 8A_1/10 + 3A_2/10 + A_3/10 + f_4/80 \tag{11d}$$
$$f_0 = A_0 + 5A_1/6 + 5A_2/16 + 5A_3/64 + 5A_4/256 + f_5/512 \tag{11e}$$
$$f_0 = A_0 + 48A_1/61 + 75A_2/244 + 5A_3/61 + 15A_4/976 + 3A_5/976 + f_6/3904, \tag{11f}$$

where

$$A_r = \frac{d^r \Delta(\alpha_i)}{d\bar{\theta}^r} \text{ at } \bar{\theta} = \pi/4$$

and

$$f_0 = f(\pi/4).$$

At successively higher limits the contribution of the residual term will tend to diminish. The values of $f(\pi/4)$ calculated from (11a) to (11f) by considering only the measurable terms in $A_1$ to $A_5$ (i.e., residual term omitted) should gradually converge to the actual value for $f(\pi/4)$.

The practical application of the proposed method of analysis to the measurement of lattice parameters may be summarized as follows.

(i) The values of $\delta(\alpha_i, \alpha_j)$ are calculated from the

![Fig. 2. Variation of the function $\delta(\alpha_i, \alpha_j)$ with $\bar{\theta}_i$ for the 311 line from a spinel oxide ($\bar{\theta}_i = 17.7^\circ$) illustrating the manner in which $f(\bar{\theta})$ may be determined by extrapolation.](image-url)
differences between the measured and derived Bragg angles of all the diffraction lines.

(ii) The variation of $\delta(a_c, a)$ with $\tilde{\theta}$ for each diffraction line ($x$, fixed) is interpolated to $\tilde{\theta} = \pi/4$ to obtain $\Delta(x)$. The values of $\Delta(x)$ and its derivatives with respect to $\tilde{\theta}$ are determined at $\tilde{\theta} = \pi/4$. These values are substituted into (11a) to (11f) in turn until a sufficiently accurate value for $f(\pi/4)$ is obtained. The criterion for doing this is considered later.

(iv) The value for $f(\pi/4)$ along with the values for $\Delta(x)$ are substituted into (7) to obtain the shift $f(\tilde{\theta})$ of each line. The true Bragg angle can therefore be evaluated along with the lattice parameter for each line.

(v) If the lattice parameters exhibit a systematic variation with $hkl$ which is greater than that expected on the basis of the precision of the data, the Bragg angles given by (iv) may be used as input data for repeating the analysis. This iteration procedure may be repeated until the lattice parameters obtained exhibit no systematic variation. Experience to date has shown that iteration is unnecessary.

Application of method to simulated data

The accuracy of the method proposed is limited by the accuracy of the procedures adopted to determine $\Delta(x)$ and $f(\pi/4)$. If a sufficiently large number of lines is measured with good precision, standard curve-fitting methods should allow accurate assessments to be made of $\Delta(x)$ and, to a lesser extent, its derivatives at $\tilde{\theta} = \pi/4$. Although the accuracy of determining derivatives by numerical methods decreases with the order of the derivative, this is compensated for in the assessment of $f(\pi/4)$ [from (11a) to (11f)] by the weighting towards the lower-order derivatives. Over the range of data typically taken in high-temperature diffractometry (e.g. $2\theta = 20$ to $130^\circ$), $\Delta(x)$ does not normally exhibit a strong non-linear angular dependence and can be justifiably expressed as a polynomial in $\theta$. Thus, the limiting factor in the determination of $f(\theta)$ will usually be the validity of using (11a) to (11f), with the residual terms omitted, to determine $f(\pi/4)$. Any error in the assessed value for $f(\pi/4)$ will introduce a tan $\theta$-dependent error in the associated value for $f(\theta)$ given by (7), which in turn corresponds to a constant fractional error in the lattice constant.

$$\Delta a/a = \text{Error } \{f(\pi/4)\}, \quad (12)$$

where $f(\pi/4)$ is in radians. To achieve an accuracy of 0.0003 A for a nominal lattice constant of 8 A (e.g. cubic spinel), the value of $f(\pi/4)$ should be accurate to within 0.002 ($^\circ$).

The effects of physical aberrations on the interpretation of the data is not considered to any great extent in the present analysis. The contribution of these over the angular range $2\theta < 130^\circ$ is generally quite small. Furthermore, given that peak angles are employed, the shift arising from dispersion is cancelled by the variation of the Lorentz factor across the profile (Wilson, 1963). Assuming, therefore, that the intensity data are corrected on a point-to-point basis for the polarization factor, the only significant physical aberrations will be refraction and variable wavelength-response effects. As both of these possess a tan $\theta$-dependent contribution to $f(\theta)$, their presence will be reflected as a constant error in the lattice parameter for all reflections. This type of physical aberration cannot be detected by the method proposed here and has to be corrected for by theoretical methods (Wilson, 1963).

The principal geometrical aberrations examined in the present work are considered to be specimen surface displacement, zero-20 error and, to a lesser extent, the combined effects of specimen transparency, flat-specimen error and axial divergence. The angular dependence of the shift in peak angle arising from these aberrations is in general a complex expression. If, however, only peak angles in excess of $5\theta$ are considered, the peak shift has approximately the same form as the centroid shift, the equations for which are well documented (Wilson, 1963). Expressions for centroid shifts have therefore been used to simulate the line shifts and how they affect the accuracy with which $f(\pi/4)$ may be determined from (11a) to (11f). The actual forms of $f(\theta)$ for the various aberrations considered are listed in Table 1 along with the corresponding expressions for $\Delta(x)$ in terms of the nominal Bragg angle.

A number of points need to be made regarding the results in this table. In the normal least-squares method of lattice-parameter determination, a form for $f(\theta)$ is fitted to the observed variation of lattice parameter. For the two most important aberrations of the present work, namely zero-20 error and specimen displacement, the corresponding variation in lattice parameter in each case is dominated by a cot $\theta$ term at lower values of $2\theta$. As already indicated, this similarity

<table>
<thead>
<tr>
<th>Aberration</th>
<th>$f(\theta)$</th>
<th>$\Delta(x(\theta))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero-20 error</td>
<td>$a_0$ sin $\theta$</td>
<td>$a_0$ sin $\theta$</td>
</tr>
<tr>
<td>Specimen-surface displacement</td>
<td>$a_1$ sin $\theta$ cos$[\theta + \pi/4]/2$</td>
<td>$a_1$ sin $\theta$ cos$[\theta + \pi/4]/2$</td>
</tr>
<tr>
<td>Flat-specimen error</td>
<td>$a_2$ (1 + cot $\theta$)</td>
<td>$a_2$ (1 + cot $\theta$)</td>
</tr>
<tr>
<td>Specimen transparency</td>
<td>$a_3$ sin$^2$ (1 + cot $\theta$)</td>
<td>$a_3$ sin$^2$ (1 + cot $\theta$)</td>
</tr>
<tr>
<td>Axial divergence</td>
<td>$a_4$ cot $\theta$ + $a_5$ (1 + cot $\theta$)</td>
<td>$a_4$ cot $\theta$ + $a_5$ (1 + cot $\theta$)</td>
</tr>
</tbody>
</table>
Table 2. Absolute errors in the lattice parameter $\Delta a$ when the values for $f(\pi/4)$ associated with each of the principal geometrical aberrations are estimated from equations (11a) to (11f) with the residual term in $f'(\pi/4)/N$ omitted

These errors correspond to the case of a nominal lattice parameter of 8 Å (e.g. spinel-type material such as MgAl$_2$O$_4$).

<table>
<thead>
<tr>
<th>Equation used</th>
<th>20-zero Specimen-displacement error (Å)</th>
<th>Flat-specimen error (Å)</th>
<th>Specimen transparency (Å)</th>
<th>Axial divergence (Å)</th>
<th>Total error (Å)</th>
<th>Total error less axial divergence (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(11a)</td>
<td>0</td>
<td>+0.0008</td>
<td>0</td>
<td>+0.0008</td>
<td>+0.0090</td>
<td>+0.0082</td>
</tr>
<tr>
<td>(11b)</td>
<td>0</td>
<td>+0.0004</td>
<td>+0.0002</td>
<td>0</td>
<td>+0.0042</td>
<td>+0.0042</td>
</tr>
<tr>
<td>(11c)</td>
<td>0</td>
<td>−0.0001</td>
<td>+0.00015</td>
<td>0</td>
<td>−0.0005</td>
<td>−0.0008</td>
</tr>
<tr>
<td>(11d)</td>
<td>0</td>
<td>−0.0002</td>
<td>−0.00014</td>
<td>0</td>
<td>−0.0004</td>
<td>−0.0004</td>
</tr>
<tr>
<td>(11e)</td>
<td>0</td>
<td>+0.0002</td>
<td>+0.00014</td>
<td>0</td>
<td>+0.00096</td>
<td>+0.0016</td>
</tr>
<tr>
<td>(11f)</td>
<td>0</td>
<td>0</td>
<td>−0.00013</td>
<td>0</td>
<td>−0.00012</td>
<td>−0.00012</td>
</tr>
</tbody>
</table>

can lead to error when estimating the lattice parameter. In the present method the angular variation of $A(\theta)$ is distinctly different for this pair of aberrations. In particular, $A(\theta)$ is constant for zero error whilst for specimen surface displacement $A(\theta)$ can exhibit a marked angular dependence. This difference is important because it reduces the likelihood of misinterpreting the relative contributions of each aberration.

It is interesting to note that axial divergence and flat-specimen error possess the same form for $A(\theta)$ with $\theta$. The use of peak angles will not affect this result at high angles (i.e. $20 > 50^\circ$). At low angles $A(\theta)$ will tend to a finite limit as $\theta \to 0$ when peak angles are employed. It should be noted also that zero-20 error and specimen surface displacement are the only aberrations which can contribute negatively to $A(\theta)$.

In the following analysis the validity of the successive approximation method for determining $f(\pi/4)$ is considered. Ideally, the residual term $f'(\pi/4)/N$ should be zero as non-zero values will be reflected directly as an error in the assessed value for $f(\pi/4)$. The actual errors in the estimated lattice parameters which follow from the omission of these residuals in (11a) to (11f) are presented in Table 2. These results correspond to the case of a nominal lattice parameter of 8 Å and a set of conditions intended to be typical of a powder diffractometer except that the specimen-surface displacement and zero-20 error are chosen slightly larger than normally encountered [i.e. zero-20 error = 0.1°, 20 error = $0.1^\circ$ 20, specimen-surface displacement = 0.5 mm, linear attenuation coefficient $\mu = 20$ mm$^{-1}$ at Cu $K_\alpha$ wavelength, radius of diffractometer $r = 173$ mm, angle of equatorial divergence $\alpha = 1^\circ$ and two sets of Soller slits of angular aperture $\Delta = 2^\circ$; (see Wilson, 1963)].

All the errors quoted in Table 2, with the exception of axial divergence, gradually decrease in going from (11a) to (11f). The combined error arising from specimen displacement and 20 error drops to the 0.0002 Å region by the fourth-order approximation, (11d). It is worth remarking that the zero error associated with the third-order approximation (11c) represents an accident of the diffractometer conditions chosen and will not always be small. To be certain of an overall accuracy of 0.0001 Å it is necessary to resort to the sixth-order approximation (11f). At this stage, however, the numerical fitting procedures are least precise. The aberrations limiting the accuracy of the method most are flat-specimen error and axial divergence. Flat-specimen error exhibits an error which converges in a slow oscillatory manner, but which can be almost eliminated by adding adjacent approximations. This does not eliminate the error from axial divergence, however, which will remain fixed at 0.0004 Å. Conversely, by choosing an equation for which the axial divergence error is zero we are left with an error of approximately 0.00015 Å owing to the flat-specimen error.

In most methods of lattice-parameter determination the contribution of axial divergence is difficult to eliminate without recourse to theoretical methods. The problem arises because the line-shift term $f(\theta)$ contains a tan $\theta$-dependent contribution which is reflected as a constant error in the lattice constant, i.e.

$$f(\theta) = a \cot 2\theta + b \cosec 2\theta = \frac{1}{2}(a + b) \cot \theta + \frac{1}{2}(b - a) \tan \theta.$$  \hspace{1cm} (13)

In the present work, also, theoretical correction procedures have been adopted. The difficulty with this approach is that accurate correction equations are only available for centroid angles (Wilson, 1963) and not for peak angles. However, as mentioned earlier, the corrections to each type of angle will be similar at high angles and the problem is therefore reduced to establishing the range of Bragg angles over which this equality is accurate.

To accomplish this the effect of convoluting an emission profile with an axial divergence profile was examined at various diffraction angles to determine the corresponding peak and centroid shifts. In this analysis the emission profile was represented by a Cauchy curve of half-height width 0.05 pm (Cu $K_\alpha$), whilst the axial divergence was simulated with equations given in Eastbrook (1952) for a pair of Soller slits of angular aperture $\Delta = 2^\circ$. From the comparison of line shifts plotted in Fig. 3, the centroid shift $\Delta \chi$ peak shift when $2\theta$ exceeds 50°. In fact, the tan $\theta$-dependent terms in each shift are approximately the same down
to $\theta = 30^\circ$. The conclusion drawn from this analysis and analyses on other combinations of profiles is that the equality between peak and centroid shift holds whenever the emission profile is significantly broader than the instrumental profile at the particular angle being considered.

On the assumption, therefore, that the axial divergence contribution can be corrected for, the absolute error in the lattice parameter obtained by the method proposed here can be reduced significantly by averaging adjacent approximations. For example, by averaging values for $f(\pi/4)$ obtained from approximations (11e) and (11f), an absolute error of $\pm 0.00002 \text{ Å}$ is attainable. Obviously this value represents an upper limit of accuracy and in practice additional errors arise from the limited precision of the data and curve-fitting procedures.

**Comparison of proposed method with least-squares method**

The equivalence of the present method with Cohen's least-squares method (see, for instance, Klug & Alexander, 1974) is demonstrated by comparing the results obtained by each method from the same set of diffraction data for a standard material with a reasonably well aligned diffractometer with Cu $K\alpha$ radiation. The cubic spinel oxide MgCr$_2$O$_4$ was chosen for this purpose as its diffraction lines are well resolved and, in most cases, sufficiently distant from neighbouring lines to allow centroid angles to be determined without the complication of overlapping lines. The benefit of using centroids is that the line shifts arising from the instrumental and physical aberrations are additive and calculable (Wilson, 1963).

The intensity data for this example were collected from a Philips powder diffractometer by step-scanning at intervals of 0.01° $2\theta$ at 100 s per step. The centroids were determined according to the equation given by Wilson (1967) with a range of integration which just encompassed the $K\alpha$ satellite lines of the emission profile. On the basis of data tabulated in Bearden (1967) and Edwards & Langford (1971) this corresponds to a wavelength of 1.54213 Å. Corrections to the measured centroids were made for flat-specimen error, specimen transparency, axial divergence, Lorentz factor, dispersion, polarization factor, refraction and wavelength-response effects (Wilson, 1963). No corrections were made for the indeterminate line shifts arising from zero-2$\theta$ error or specimen-surface displacement.

The values of these corrected centroids $2\theta_c$ are presented together with the associated values of the lattice parameters in Table 3. The errors in $2\theta_c$ given in this table represent the precision of the centroid measurement arising from intensity statistics and were obtained from the expression

$$
\sigma^2(2\theta_c) = \sum_i \left( \frac{\partial^2 \theta_c}{\partial I_i} \right)^2 \sigma^2(I_i)
$$

(Wilson, 1967), where the terms $I_i$ represent the measured X-ray intensities and $\sigma^2(I_i)$ is the variance arising from intensity statistics. Lattice parameters determined with Cohen's least-squares method are also presented in Table 3 for residual aberration functions $f(\theta)$ corresponding to

1. specimen surface displacement and zero-2$\theta$ error [i.e. $f(\theta) = p + q \cos \theta$];
2. zero-2$\theta$ error only [i.e. $f(\theta) = p$];
3. specimen surface displacement only [i.e. $f(\theta) = q \cos \theta$].

The best fit in this analysis was obtained with $f(\theta) = -0.0082 - 0.0105 \cos \theta$ and a lattice parameter of 8.3369 (1) Å. It should be noted, however, that the mean-square fit obtained by assuming a zero-2$\theta$ error alone was only marginally greater, but gave a value for the lattice parameter of 8.3372(1) Å with $f(\theta) = -0.0188 (\cos \theta)$. In both cases the variation of lattice parameter with $hkl$ does not exhibit any significant trends outside the limits set by the statistical scatter of the data. In fact, the data are not extensive enough or of sufficient accuracy to distinguish between these two forms chosen for $f(\theta)$. Thus, although the precision here is $\sim 0.0001$ Å, the accuracy of any lattice parameter can, at best, only be $\sim 0.0003$ Å.

The analysis of the MgCr$_2$O$_4$ data by the method proposed here is summarized in the last column of Table 3. As the diffractometer was reasonably well aligned the measured angles represented by $\alpha_i(i = 1$ to
Table 3. Corrected 2θ centroid values for the cubic spinel oxide MgCr₂O₄ along with lattice parameters calculated (i) from the centroid values, (ii) by Cohen's method using different assumed forms for f(θ) and (iii) by the proposed method of this paper.

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>Corrected centroid (2θ)</th>
<th>Lattice parameter (i)</th>
<th>Zero error + Displacement</th>
<th>Zero error only</th>
<th>Displacement only</th>
<th>Lattice parameter (iii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>35.7318(2)</td>
<td>8.32878(5)</td>
<td>8.33699</td>
<td>8.33725</td>
<td>8.33677</td>
<td>8.33723</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2</td>
<td>37.3802(2)</td>
<td>8.33904(4)</td>
<td>8.33769</td>
<td>8.33706</td>
<td>8.33657</td>
<td>8.33724</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>43.4350(2)</td>
<td>8.33048(4)</td>
<td>8.33703</td>
<td>8.33734</td>
<td>8.33680</td>
<td>8.33723</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>47.5632(5)</td>
<td>8.33089(8)</td>
<td>8.33677</td>
<td>8.33709</td>
<td>8.33652</td>
<td>8.33724</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>2</td>
<td>53.9000(10)</td>
<td>8.33186(14)</td>
<td>8.33689</td>
<td>8.33724</td>
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<td>8.33725</td>
</tr>
<tr>
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<td>1</td>
<td>1</td>
<td>57.4633(2)</td>
<td>8.33221(2)</td>
<td>8.33682</td>
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<td>8.33653</td>
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<td>63.1107(2)</td>
<td>8.33281(2)</td>
<td>8.33687</td>
<td>8.33726</td>
<td>8.33657</td>
<td>8.33725</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>1</td>
<td>82.6990(10)</td>
<td>8.33404(8)</td>
<td>8.33670</td>
<td>8.33715</td>
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<td>8.33711</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>1</td>
<td>90.5600(10)</td>
<td>8.33462(7)</td>
<td>8.33687</td>
<td>8.33733</td>
<td>8.33651</td>
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<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>95.4720(10)</td>
<td>8.33472(7)</td>
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<td>8.33721</td>
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<tr>
<td>8</td>
<td>4</td>
<td>0</td>
<td>111.6540(10)</td>
<td>8.33571(5)</td>
<td>8.33710</td>
<td>8.33757</td>
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<tr>
<td>9</td>
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<td>1</td>
<td>123.868(2)</td>
<td>8.33584(7)</td>
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<tr>
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<td>4</td>
<td>4</td>
<td>130.006(5)</td>
<td>8.3359(2)</td>
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<td>8.33641</td>
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<tr>
<td>9</td>
<td>3</td>
<td>3</td>
<td>133.964(5)</td>
<td>8.3360(2)</td>
<td>8.33672</td>
<td>8.33712</td>
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<td>8.33719</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0</td>
<td>141.230(10)</td>
<td>8.3364(3)</td>
<td>8.33695</td>
<td>8.33732</td>
<td>8.33667</td>
<td>8.33722</td>
</tr>
</tbody>
</table>

Mean lattice parameter 8.33686(11) 8.33723(12) 8.33656(16) 8.33723(7)

N) satisfy the conditions α ≈ θ. The interpolation of δ(αi, αj) and the analysis of M(αj), therefore, was carried out in terms of α by fitting a fifth-order polynomial with a standard least-squares method. In the fitting procedure a weighting scheme was employed in which the weighting function ωj was given by

\[ \omega_j = \frac{1}{\sigma^2(F_j)} \]

where \(\sigma(F_j)\) is the estimated standard error of the function being fitted.

The values established for f(π/4) from the above fitting procedure with (11a) to (11f) are presented in Table 4. These values vary very little and rapidly converge to a constant value beyond the third-order approximation. In fact, the difference between the first- and sixth-order approximations is only 0.0007 (°θ), which corresponds to a change in mean lattice parameter of <0.0001 Å. The lattice parameters quoted in Table 3 correspond to the values given by using the fourth-order approximation for f(π/4). These exhibit no significant trends with hkl and are remarkably consistent with the lattice parameters given by Cohen's least-squares method when f(θ) is chosen to be constant (i.e. zero-2θ error only). The actual variation of f(θ) given by the present method is compared in Fig. 4 with the variations obtained from Cohen's method by assuming zero-2θ error only and zero-2θ error + specimen-surface displacement.

The conclusion drawn from this comparison is that the method proposed here is valid and gives results whose precision is equivalent to standard least-squares methods under near-ideal circumstances. There is also the additional benefit that the method does not require a specific analytic form to be assigned to the line-shift function f(θ). This property is particularly valuable when f(θ) is either unknown or possesses a complex angular dependence. More often than not the effectiveness of the present fitting procedures obviates the need for testing for residual systematic

Table 4. Values of f(π/4) in °θ for MgCr₂O₄ data calculated from equations (11a) to (11f), but with the residual term f(π/4)/N omitted from the equation

<table>
<thead>
<tr>
<th>Equation employed</th>
<th>f(π/4) (°θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11(a)</td>
<td>-0.01915</td>
</tr>
<tr>
<td>11(b)</td>
<td>-0.01893</td>
</tr>
<tr>
<td>11(c)</td>
<td>-0.01867</td>
</tr>
<tr>
<td>11(d)</td>
<td>-0.01847</td>
</tr>
<tr>
<td>11(e)</td>
<td>-0.01840</td>
</tr>
<tr>
<td>11(f)</td>
<td>-0.01841</td>
</tr>
</tbody>
</table>

Fig. 4. A comparison of the line-shift functions f(θ) obtained from the present method with the variations given by Cohen's least-squares method assuming f(θ) arises from (i) zero-2θ error only and (ii) zero-2θ error + specimen-surface displacement.
Table 5. Comparison of measured angles (2\(\theta\)), corrected Bragg angles \(2\theta\) and associated lattice parameters \(a\) for some of the lines obtained from the superconducting oxide \(\text{LiTi}_2\text{O}_4\) using a low-temperature attachment with \(\text{Cu K}\alpha\) radiation

The errors given for \(2\theta\) represent the effect of counting statistics. The errors given for the corrected \(2\theta\) angles reflect the combined effect of counting statistics and the accuracy with which \(f(\pi/4)\) was determined.

The table lists measured angles, corrected angles, and lattice parameters for various reflections of \(\text{LiTi}_2\text{O}_4\) using low-temperature attachment.

Some features of the practical application of the proposed method

The method proposed here was developed to overcome some of the problems of determining lattice parameters under the adverse conditions encountered in high- and low-temperature powder diffractometry. In this section, therefore, the results considered were collected from a low-temperature attachment (viz. an Oxford Instruments Cryostat) fitted on to a Philips vertical powder diffractometer with the superconducting spinel oxide \(\text{LiTi}_2\text{O}_4\) as the specimen and \(\text{Cu K}\alpha\) as the radiation. The actual intensity measurements were recorded by step-scanning at intervals \(\Delta 2\theta = 0.01\) or \(0.02\)° over the peaks at 100 s per step. Each peak angle was determined as part of a standard data-reduction program in which a quartic polynomial is fitted to the tops of the peaks (Baker, George, Bellamy & Causer, 1968). Some of these results are tabulated in Table 5 along with the standard errors arising from counting statistics and the corresponding corrected Bragg angles and lattice parameters.

One of the most significant advantages of the method which is illustrated in this table is that the peak angles \((2\alpha)\) are measured relative to the peak position of the strongest line (i.e. 311) and not the mechanical zero of the diffractometer. In these results \(2\alpha=0\) corresponds to a \(2\theta\) angle of \(\sim 35.4\)°. Under these circumstances the interpolation and fitting procedures have to be carried out in terms of the mean derived angle \(\bar{\psi}_j\) of each profile.

In considering the reliability of any fitting procedure it is worth noting that \(\delta(\alpha_i, \alpha_j)\) has the same value at \(\bar{\psi}_j=0\) irrespective of the value for \(\alpha_i\).

\[
\lim_{\bar{\psi} \to 0} \delta(\alpha_i, \alpha_j) = f(0).
\]

Thus, any curve fitting to \(\delta(\alpha_i, \alpha_j)\) should be carried out under the constraint that for each \(\alpha_i\) the fitted curve should start at the same value when \(\bar{\psi}_j=0\). Generally speaking this is so and an extremely good fit to \(\delta(\alpha_i, \alpha_j)\) can be obtained by using a fifth-order polynomial as illustrated in Fig. 5 for the 400 line from \(\text{LiTi}_2\text{O}_4\). The error bars \(\pm \sigma(\delta)\) given in this graph for the measured values of \(\delta(\alpha_i, \alpha_j)\) were calculated from the precision of the measurements of \(\alpha_i\) and \(\alpha_j\) according to the relationship

\[
\sigma(\delta) = \frac{\sigma(\varphi) \sin 2\theta_i}{2 \sin \varphi},
\]

where \(\sigma(\varphi)\) is the standard error in \(\varphi = \alpha_j - \alpha_i\). From this equation it is clear that \(\delta(\alpha_i, \alpha_j)\) is less sensitive to errors as \(2\theta_i\) approaches \(0\) or \(180\)° and when \(\varphi = 90\)°. This behaviour is reflected in Fig. 6 by the error bars which are large for closely spaced peaks and small for widely spaced peaks. Because of the variation in error size, each value of \(\delta(\alpha_i, \alpha_j)\) is given a weight of \(1/\sigma^2(\delta)\) in the polynomial fitting procedure.

The error \(\sigma(\delta)\) also represents the error \(\sigma(\psi)\) in the associated derived Bragg angle \(\psi\). Thus for a pair of lines with a reasonable separation (e.g. \(2\alpha_i = 30\)° and \(2\alpha_j = 130\)°), the errors \(\sigma(\delta)\) and \(\sigma(\psi)\) will be approximately the same as the errors in the original experimental values for \(\alpha_i\) and \(\alpha_j\). To a first-order approximation, therefore, the uncertainty \(\sigma(D)\) in the value for \(D(\alpha_i)\) found by interpolation will be in the vicinity of \(\sigma(\alpha_i)/\sqrt{n-2}\), where \(\alpha(\alpha)\) is the average error in the peak-angle measurements and \(n\) is the number of peaks measured.

The practice adopted to determine which value for \(f(\pi/4)\) to use in evaluating \(f(\theta)\) is to consider the values

\[
\delta(\alpha_i, \alpha_j) (\text{°})
\]

\[
\alpha_i
\]

Fig. 5. An illustration of the fit obtained with a fifth-order polynomial to represent the measured variation of \(\delta(\alpha_i, \alpha_j)\) obtained from the results in Table 5 for the 400 line of \(\text{LiTi}_2\text{O}_4\).
obtained for each successive approximation [i.e. (11a) to (11f)]. In most instances \( f(\pi/4) \) stabilizes within a range of 0.002° without averaging adjacent values by the fourth-order approximation as shown in Table 4. If this uncertainty is combined with the uncertainty in each value for \( \Delta(z_i) \) the associated uncertainty in the lattice parameter \( \sigma(a) \) will be given approximately by

\[
\sigma(a)/a \approx \sigma(z) + \sigma[f(\pi/4)].
\]

For a set of 27 measurements in which each peak angle is located with an uncertainty of 0.01° [i.e. \( \sigma(z) = 0.005° \)] and \( f(\pi/4) \) is determined to within 0.002°, the expected accuracy will be

\[
\sigma(a)/a \approx 1 \text{ part in } 20000.
\]

If the original measurement uncertainty is 0.001°, the value of \( \sigma(a)/a \) reduces to

\[
\sigma(a)/a \approx \sigma[f(\pi/4)] \approx 1 \text{ part in } 35000.
\]

The scatter of the lattice-parameter values given in Table 5 along with the errors of measurement (calculated with more rigorous statistical techniques) confirm the order-of-magnitude error calculations given above. In this method the limiting accuracy of \( 'a' \) is determined by the accuracy with which \( f(\pi/4) \) may be evaluated and not by the precision of the original peak-angle measurements.

It should be noted that the forms for \( f(\theta) \) generally obtained by the present method are consistent with the types of variation expected for powder diffractometers. The variation of \( f(\theta) \) obtained for the \( \text{LiTi}_2\text{O}_4 \) sample is compared in Fig. 6(a) with the form expected for the centroid shift of all the instrumental aberrations with the exception of zero-2\( \theta \) error and specimen-surface displacement. The plot in Fig. 6(b) of the difference between these values for \( f(\theta) \) is substantially a linear function of \( \cos \theta \), thus indicating that the difference probably arises from zero-2\( \theta \) error and specimen-surface displacement. The departure corresponding to \( 2\theta < 50° \) probably arises because the peak shift and centroid shift do not possess the same angular dependence at low angles.

Finally, it is worth commenting that the proposed method can compensate for apparent line shifts arising from the overlapping of lines provided only a small proportion of results are affected in this way. When a peak value \( x_i \) suffers such a shift the function \( \delta(x_i, x_j) \) will still vary with \( x_j \) in a uniform manner as all pairs will be affected by this shift. The variation of \( \Delta(z_j) \), on the other hand, will exhibit irregularities at those lines affected by overlap. However, if most of the lines are free of overlap a reasonably accurate assessment of \( f(\pi/4) \) can be obtained. Consequently, the effects of overlap on particular lines will be reflected in the measured \( f(\theta) \) as departures from the main trend of unaffected results.

References