Systematic Errors in Precision Lattice-Parameter Determination of Single Crystals Caused by Asymmetric Line Profiles

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Abstract

The convolution of the various contributions to X-ray intensity distribution curves measured in lattice-parameter determination leads to peak shifts and, hence, to systematic errors in the case that at least one of the contributing curves is asymmetric. For perfect crystals, depending on the collimator divergence, this effect may reach the order of magnitude of the refraction correction. It is caused by the asymmetry of the spectral distribution curve, which includes intrinsic asymmetry, dispersion and angle dependence of intensity (ADI). For imperfect crystals characterized by orientation and interplanar-spacing distributions, the distribution curves should be measured in order to correct accurately the peak shift. Examples of simulation calculations are given for Si, Cu Kα1, Bond method for various reflections of perfect crystals and for crystals having orientation distributions, 444 reflection.

1. Introduction

The measurement of absolute diffraction angles for an X-ray emission line is the most commonly applied procedure of precision lattice-parameter determination of single crystals. With the very familiar Bond method, measurements can be repeated down to 1 in $10^7$ (Bond, 1960; Baker, George, Bellamy & Causer, 1968; Grosswig, Hartwig, Alter & Christoph, 1983). Therefore, any systematic errors should be kept smaller or be known exactly with the same accuracy in order to be able to correct correctly the experimental values. Usually corrections due to refraction and to the geometric errors of axial beam and net-plane tilts as well as axial beam divergence are taken into account (Bond, 1960; Burke & Tomkeiiff, 1968, 1969; Gruber & Black, 1970; Nemiroff, 1982; Berger, 1984a).

Some uncertainties result from the properties of the X-ray lines, whose absolute peak wavelengths are known only with an accuracy of 1 in $10^6$ (Bearden, 1967; Hart, 1981). Hence, the lattice parameters must be given with respect to the used X-ray line and wavelength value.

The problems connected with the natural X-ray line width can be overcome in principle by making use of crystal-collimated radiation. The non-dispersive lattice comparator techniques (Ando, Bailey & Hart, 1978; Hart, 1981) need special arrangements for different specimens and reflections and are therefore preferably limited to serial studies of one kind of crystal. The four-crystal monochromator combined with a Bond diffractometer (Bartels, 1983) can be applied without these restrictions. However, the equipment is sophisticated, and complications come from the resulting low intensities.

Because of the advantages of simple and universal diffractometer techniques like the Bond method, an alternative procedure is the exact correction of the errors due to the broad and asymmetric X-ray emission lines. Up to now, only the peak shift due to distortions of the spectral line has been considered, with some contradictions. The distortion is caused mainly by the Lorentz–polarization (LP) factor (Bond, 1960, 1975; Segmüller, 1970; Okazaki & Ohama, 1979; Urbanowicz, 1981). A few other factors for line distortion have been mentioned by various authors, predominantly relating to the diffractometry of polycrystalline samples (Ladell, 1961; Short & Kelly, 1973; Delhez, Mittemeijer, de Keijser & Rozendaal, 1977; Bradaczek, Leps & Uebach, 1982; Berger, 1984a). The distortion of the spectral line by ‘dispersion’ as considered in powder diffractometry (Pike, 1959; Ladell, Mack, Parrish & Taylor, 1959) does not shift the peak and was therefore claimed to be negligible in methods evaluating the peak positions (Bond, 1960; Segmüller, 1970; Hart, 1981).

An error that has not yet been discussed in the literature is caused by the convolution of the various single distribution functions composing the measured intensity profiles. The convolution of curves, from which at least one is asymmetric, may lead to an appreciable peak shift. It is the aim of this paper to discuss this error including the exact spectral line distortion and to give examples to show its order of magnitude. Since it is not possible to calculate the correction by means of explicit expressions, they can only be estimated by means of simulation calculations for concrete experimental conditions. The cases of perfect as well as of imperfect crystals will be discussed.
2. Description of the intensity distribution functions

The intensity distribution function of a single-crystal X-ray reflection can be described by convolution of the following single distribution functions:

(1) intrinsic diffraction pattern,
(2) orientation distribution,
(3) interplanar-spacing (strain) distribution,
(4) spectral distribution,
(5) distribution produced by axial (vertical) beam divergence,
(6) collimator function (horizontal divergence distribution).

In the following discussion it will be assumed that the influences of functions (1) and (5) are negligible.

Consider now perfect crystals. Then we have

\[ I_{s,c}(y) = \int_{-\infty}^{\infty} C(x)S(x-y)dx \]  

\[ S(\lambda) = \sum_{j=1}^{4} Q_j \left[ 1 + \left( \frac{2}{w_j} \right) (\lambda - \lambda_j)^2 \right]^{-1} \]  

(\( \lambda \) is the wavelength parameter, \( \lambda_j \) the maximum, \( w_j \) the halfwidth, \( Q_j \) the relative peak height of an intrinsic single line; \( j = 1, 2 \) for \( K\alpha_1 \), \( j = 3, 4 \) for \( K\alpha_2 \).

Going from the wavelength to the diffraction angle scale, we get exactly

\[ (2/w_j)(\lambda - \lambda_j) = (2\lambda_j/w_j)(\cos x + \sin x \cot \theta_j - 1) \]  

with

\[ x = \theta - \theta_j \]

This effect of dispersion makes the spectral asymmetry increase and, therefore, it cannot be neglected in our connection.

The third effect contributing to the asymmetry of the spectral line is the distortion caused by the angle dependence of intensity (ADI). Its main contribution is the Lp factor, but the full expression for the integrated reflection should be used considering all the angle-dependent factors. The \( \theta \) dependence of the integrated reflection (for constant interplanar spacing \( d \)) may be generally written as

\[ R(\theta) = R(\theta_M) + x\partial R(\theta_M)/\partial \theta = R(\theta_M)(1 + U_\lambda x) \]  

with

\[ x = \theta - \theta_M \]

(\( \theta \) is the diffraction angle; the index \( M \) of the angle variables stands for the maximum of the corresponding curve). The coefficients like \( U_\lambda \) will be called ADI coefficients. For nearly perfect crystals the formula for the integrated reflection according to the dynamic theory is to be used, for strongly distorted crystals the formula for the ‘mosaic’ crystal may be valid (Hirsch & Ramachandran, 1950).* Because the intensity registered in the detector is attenuated by absorption in the tube target, in air and other materials in the beam path and is influenced by the detector efficiency, the \( \lambda \) and, therefore, \( \theta \) dependence of these absorption processes must be considered, too (Wilson, 1958). Furthermore, if the irradiated area on the crystal surface is kept constant, as done, for example, in the Soller-slit method (Berger, 1984b), the intensity is proportional to \( \sin (\theta + \phi) \) (\( \phi \) is the angle between crystal surface and reflecting net planes). In both cases the intensity is to be multiplied by a factor and, hence, the corresponding ‘instrumental’ ADI coefficient is to be added to the above ‘crystal-specific’ \( U_\lambda \) values.

Some examples of ADI coefficients are given in Table 1. Besides the Lp factor the angle dependence of the asymmetry of reflection may also markedly contribute to the resulting \( U_\lambda \) values (Fig. 1).

If separate spectral lines (for example, for \( K\alpha_1 \) and \( K\alpha_2 \) radiation) are to be related, the exact ratio of the two integrated reflections, \( R_{\lambda_1}/R_{\lambda_2} \), should be used. The intensity variation over the two curves is described by the ADI coefficients \( U_{\lambda_1} \) and \( U_{\lambda_2} \), respectively.

The final spectral distribution function \( S \) on the angle scale can be written as

\[ S(\theta) = \sum_{j=1}^{4} P_j Q_j \left[ 1 + \frac{2}{w_j} (\theta - \theta_j)^2 \right]^{-1} \]

\[ x \in [\cos(x - z_j) + \sin(x - z_j)\cot \theta_j - 1] \]

with

\[ P_1 = P_2 = 1 + U_{\lambda_1} (x - z_1), \]

\[ P_3 = P_4 = (R_{\lambda_2}/R_{\lambda_1})/[1 + U_{\lambda_2} (x - z_3)], \]

\[ z_j = \theta_j - \theta_0 \]

(\( \theta_0 \) is any fixed point on the \( \theta \) scale).

The collimator function may be described by a trapezium

\[ C(x) = 1 - f/\delta_2 \]

with

\[ f = \begin{cases} 
-1 \quad \text{for} \quad -\delta_2 \leq x \leq -\delta_1 \\
\delta_1 \quad \text{for} \quad -\delta_1 \leq x \leq \delta_1 \\
x \quad \text{for} \quad \delta_1 \leq x \leq \delta_2 
\end{cases} \]

*Explicit formulae for all the intensity values and ADI coefficients used in this paper have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42570 9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
Table 1. ADI coefficients $U_\lambda$ for Si, (111) surface, Cu $K\alpha_1$

Instrumental ADI coefficients calculated for: 40 kV, take-off angle of focus 6°, Be window, air path 1000 mm, scintillation counter.

<table>
<thead>
<tr>
<th>Reflection</th>
<th>$U_\lambda$</th>
<th>$\phi_M$ pos.</th>
<th>$\phi_M$ neg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>444</td>
<td>444</td>
<td>-1.049</td>
<td>-1.049</td>
</tr>
</tbody>
</table>

Instrumental beam path absorption constant irradiated area

<table>
<thead>
<tr>
<th>Reflection</th>
<th>$U_\lambda$</th>
<th>$\phi_M$ pos.</th>
<th>$\phi_M$ neg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>444</td>
<td>444</td>
<td>-1.049</td>
<td>-1.049</td>
</tr>
</tbody>
</table>

Crystal specific

<table>
<thead>
<tr>
<th>Reflection</th>
<th>$U_\lambda$</th>
<th>$\phi_M$ pos.</th>
<th>$\phi_M$ neg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>444</td>
<td>444</td>
<td>-1.049</td>
<td>-1.049</td>
</tr>
</tbody>
</table>

Mosaic crystal

<table>
<thead>
<tr>
<th>Reflection</th>
<th>$U_\lambda$</th>
<th>$\phi_M$ pos.</th>
<th>$\phi_M$ neg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>444</td>
<td>444</td>
<td>-1.049</td>
<td>-1.049</td>
</tr>
</tbody>
</table>

Table 2. Numerical values as used for simulation calculations, Si, Cu $K\alpha$, Bond method

<table>
<thead>
<tr>
<th>Spectral parameters:</th>
<th>$\lambda$ (nm)</th>
<th>$\phi_M$ (nm)</th>
<th>$Q_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>j</td>
<td>$\lambda_j$ (nm)</td>
<td>$\phi_j$ (nm)</td>
<td>$Q_j$</td>
</tr>
<tr>
<td>1</td>
<td>0.189</td>
<td>1.721</td>
<td>6.475</td>
</tr>
</tbody>
</table>

Intensity ratios and ADI coefficients (including instrumental; for conditions see Table 1):

<table>
<thead>
<tr>
<th>Reflection</th>
<th>$U_\lambda$</th>
<th>$U_\phi$</th>
<th>$R_{s2}/R_{s1}$</th>
<th>$U_\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>333</td>
<td>-2.300</td>
<td>-2.245</td>
<td>1.006</td>
<td></td>
</tr>
<tr>
<td>533, $\phi_M$ pos.</td>
<td>1.797</td>
<td>1.864</td>
<td>0.988</td>
<td></td>
</tr>
<tr>
<td>533, $\phi_M$ neg.</td>
<td>1.196</td>
<td>1.266</td>
<td>0.992</td>
<td></td>
</tr>
<tr>
<td>444</td>
<td>4.813</td>
<td>5.277</td>
<td>0.934</td>
<td>-0.189</td>
</tr>
</tbody>
</table>

($\delta_1-\delta_2$ is the maximum horizontal divergence of the collimator).

An imperfect crystal may additionally have orientation and interplanar-spacing distributions. These distribution curves must be measured experimentally. The measured curves are also influenced by the ADI. For the interplanar-spacing distribution, the $\theta(d)$ dependence of the integrated reflection holds (for constant $\lambda$). In the case of the orientation distribution, the dependence of $\phi$ of some factors in the expression for the integrated reflection (for constant $\theta$) must be calculated (Berger, 1984a) in order to obtain the true intrinsic distribution functions. The corresponding ADI coefficients $U_\phi$ and $U_\phi$, respectively, deviate analogously to (4). However, if the orientation and interplanar-spacing distributions are measured using the same conditions as employed for the lattice-parameter measurement, the curve distortions do not need to be calculated explicitly. On the other hand, the correction procedure is to apply if the intrinsic distribution functions are to be determined.

In order to simulate the influence of an orientation distribution, the spectral distribution as given above is convoluted with an orientation distribution function $O(x)$:

$$I_{S,O}(y) = \int_{-\infty}^{\infty} O(x)S(x - y) \, dx.$$  (7)

The intrinsic orientation function may be a Lorentzian. Hence, the function $O(x)$ is expressed by

$$O(x) = \frac{1 + U_\phi x}{1 + (4x^2/w_0^2)}.$$  (8)

($w_0$ is the halfwidth of the intrinsic orientation distribution curve).

3. Examples and discussion

The peak shifts of intensity distribution curves were calculated for Si, Cu $K\alpha_1$ radiation, as functions of the collimator-curve halfwidth for perfect crystals according to (1) (Figs. 2 and 3) and of the orientation distribution curve for imperfect crystals according to (7) (Fig. 4), respectively. The numerical values of the parameters used for the simulation calculation are given in Table 2.

The contributions of the single factors influencing the asymmetry of the spectral distribution curve to the peak shift for a perfect crystal (Fig. 2) were computed by neglecting this contribution and evaluating the difference to the whole error. Except at very small $w_\phi$, the contribution of the intrinsic spectral asymmetry of the $K\alpha_1$ line is predominant.

The peak shifts as shown in Figs. 2 and 3 are the real corrections $\Delta\theta$ to be subtracted from the experimental diffraction angles of silicon for the given reflections. Fig. 3 shows the comparison with experimental values measured with extremely high collimator divergences.
in order to prove distinctly the peak shifts. For usual collimator divergences the corrections may reach the order of magnitude of the refraction correction. They may be neglected only for very small collimator divergences if values of medium accuracy (error > 1 in 10^6) are sufficient.

Because the material-specific ADI contribution is comparatively small and varies slowly with the collimator divergence, the given plots may be used also to estimate the corrections for other nearly perfect crystals. On the other hand, the ADI coefficients may reach rather high values, for example, for high reflection asymmetry (Fig. 1), which is applied to

Fig. 2. Shifts \( \Delta a \) (lattice parameter) and \( \Delta \theta \) the \( \mathrm{K}_{\alpha_1} \) peak caused by convolution of spectral distribution and collimator curves vs halfwidth \( w_c \) of the collimator curve, Si, (111) surface, Cu \( \mathrm{K}_{\alpha} \), Bond method. —— Whole error; —— only intrinsic spectral asymmetry; —— only ADI; —— only \( \mathrm{K}_{\alpha_2} \) contribution; —— only dispersion. (a) 333 reflection; (b) 533 reflection; (c) 444 reflection.

Fig. 3. Comparison of experimental (circles) and calculated (full line) shifts \( \Delta a \) (lattice parameter) and \( \Delta \theta \) the \( \mathrm{K}_{\alpha_1} \) peak caused by convolution of spectral distribution and collimator curves vs halfwidth \( w_c \) of the collimator curve, Si, symmetric 444 reflection, Cu \( \mathrm{K}_{\alpha} \), Bond method. The triangular shape of the collimator curve for the large slit widths was realized by oscillating the X-ray tube during the measurement.

Fig. 4. Shifts \( \Delta a \) (lattice parameter) and \( \Delta \theta \) the \( \mathrm{K}_{\alpha_1} \) peak caused by convolution of spectral and orientation distribution (Lorentzian) curves vs halfwidth \( w_o \) of the orientation distribution curve, Si, symmetric 444 reflection, Cu \( \mathrm{K}_{\alpha} \), Bond method.
get additional information (Wołczyr, Pietraszko & Łukaszewicz, 1980).

The corrections due to the convolution of spectral with orientation and interplanar-spacing distributions, respectively, of imperfect crystals may be appreciable, especially if these distributions also have asymmetric tails. The plot given in Fig. 4 may be used to estimate roughly the peak shift for symmetric distribution curves. The peak shifts are further enhanced by convolution with the collimator function.

With the usual methods of lattice-parameter determination the angle difference of the maxima of two intensity distribution curves is measured. In general, the peak shifts $\Delta \theta_1$ and $\Delta \theta_2$ of the two curves are different so that the diffraction angle correction is

$$\Delta \theta = \frac{1}{2}(\Delta \theta_1 + \Delta \theta_2).$$

The orientation distribution curves have the same sign of asymmetry on a common angle scale for the two beams, i.e. opposite signs on the two $\theta$ scales. Hence, the spectral distributions are convoluted with orientation distributions of opposite signs in the two directions. In this way, the influence of strongly asymmetric orientation distributions is eliminated. On the other hand, because asymmetric interplanar-spacing distributions have the same signs on the $\theta$ scales of the two beams, the resulting peak shifts may be especially large.

For perfect crystals and Cu K$\alpha$ radiation, the corrections due to the convolution of spectral distribution and collimator functions can be easily calculated using the procedure as given above. It should be mentioned that for other characteristic radiations, such as Fe K$\alpha$, Co K$\alpha$, the intrinsic halfwidths as well as the asymmetries and therefore the peak-shift corrections are essentially larger than for Cu K$\alpha$. Since these lines have a more complicated structure (Finster, Leonhardt & Meisel, 1971; Tsutsumi & Nakamori, 1973), an appropriate analytic description of the spectra must still be found.

The examples and estimations show that already in the case of moderately distorted crystals lattice parameters may be inaccurate to higher values than claimed up to now, as far as corrections for orientation and interplanar-spacing distributions have not been carried out. It must be pointed out that this is true also for methods of lattice-parameter determination that nearly eliminate the spectral distribution. The exact correction requires sophisticated computational procedures including detailed information on the shape of the single intensity-distribution curve contributions. Consequently, exact lattice-parameter determinations of imperfect crystals appear to be restricted to measurements in connection with a comprehensive perfection analysis.

References


