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Measurement and Correction of Secondary Extinction in CaF_2 by means of Synchrotron X-ray Diffraction Data

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Abstract

The analysis of the full-width at half-maximum (FWHM) of X-ray diffraction profiles measured with monochromatic synchrotron radiation enables the evaluation of the mosaic spread of the sample. This method presupposes the high collimation of synchrotron radiation (FWHM $\sim 20''$ of arc). As an example the results from a CaF_2 crystal sphere (90 μm diameter) are presented. The reflections strongly affected by extinction show a significantly greater FWHM, thereby indicating at once the need for an extinction correction. A mosaic spread of 75(3)″ of arc was determined from the FWHM of all reflections recorded in the step-scan mode, which was used to correct the secondary extinction and to estimate the radius R of the mosaic blocks [$R = 4\,(1)$ μm].

Introduction

X-ray diffraction experiments can be interpreted by the dynamical or by the kinematical theory. The dynamical theory is used for perfect crystals whereas the kinematical theory is suitable for strongly imperfect crystals because it neglects the multiple scattering. The crystal model for the latter theory is the mosaic crystal (Darwin, 1922). The integrated reflection power R can be calculated by both theories. In general, the theoretical results are related to the experimental value R_m by

$$R_{\text{kin}} > R_m > R_{\text{dyn}}$$

because R_m is a function of the degree of crystal imperfection. The dynamical value approaches the kinematical one if the thickness of the crystal tends to zero. In the case of large single crystals with plane surfaces the kinematical approximation can be used for grazing incidence (Mathieson, 1977*a*). In general, the kinematical theory can be used for crystals with diameter smaller than the extinction length L (Zachariasen, 1945).

$$L = r_0^{-1} V_c [|F_h| \lambda C_p]^{-1} \qquad (1)$$

with r_0 the classical electron radius, V_c the volume of the elementary cell, λ the wavelength, F_h the structure amplitude, C_p the polarization factor (1 or $\cos 2\theta_B$ for polarization perpendicular and parallel to the diffraction plane, respectively, θ_B is the Bragg angle).

In crystal structure analysis one is anxious to reduce extinction and there are different ways to achieve this experimentally:

1. Use of short wavelengths (γ-rays) (Schneider, 1983).
2. Measurements in parallel-polarization geometry with Bragg angles near $\pi/4$ (Mathieson, 1977*b*).
3. Reduction of crystal size (Bachmann, Kohler, Schulz, Weber, Kupcik, Wendschuh-Josties, Wolf & Wulf, 1983).

The secondary extinction is caused by the mosaicity of the sample; this latter property is characterized by the spread described by the orientation distribution function. If a Gaussian distribution is assumed, the so-called extinction coefficient g is related to the mosaic spread w_s (the FWHM of the distribution function) by

$$g = [\ln 2/(2\pi)]^{1/2} w_s^{-1}. \qquad (2)$$

If g is known, the integrated reflection power R_m can

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be calculated from the kinematical value R_{kin}

$$R_m = R_{kin} \exp(-gR_{kin}).$$

In structure refinements with X-ray diffraction data the extinction coefficient (and conversely the mosaic spread) is determined from the measured intensity maxima according to various models (Zachariasen, 1967, 1968; Becker & Coppens, 1974, 1975; Cooper & Rouse, 1970). The aim of the present work is an experimental measurement of the mosaic spread prior to the refinement and without any additional experiments (such as rocking-curve measurements with a double-crystal diffractometer) and the correction of the secondary extinction caused by this mosaic spread.

Basic considerations

In single-crystal diffractometry the reflection profile is affected by the divergence of the incident radiation, the wavelength range and the properties of the sample. If the FWHM of the reflection profile, w, is plotted against the Bragg angle θ_B the following dependence is found:

$$w^2 = A^2 + B^2 \tan^2 \theta_B. \qquad (3)$$

In the present study the coefficient B is mainly determined by the relative wavelength range $\Delta\lambda/\lambda$ and A is to first approximation a function of the beam divergence w_d and the mosaic spread w_s, which are independent of the Bragg angle θ_B. The deconvolution of beam divergence and mosaic spread requires a knowledge of both distribution functions.

The beam divergence can be determined by measuring reflection profiles of a perfect crystal, *e.g.* silicon or some other crystals free of dislocations. The FWHM of the diffraction profile as measured with a nearly monochromatic beam, $\Delta\lambda/\lambda \simeq 0$, can be given by

$$w^2 = [(\Delta d/d)^2_{dyn} + (\Delta d/d)^2_{strain} + (\Delta\lambda/\lambda)^2] \tan^2 \theta_B + w_s^2 + w_d^2. \qquad (4)$$

$(\Delta d/d)_{dyn}$ is the virtual lattice-parameter variation due to the FWHM of the rocking curve of a perfect crystal given by the dynamical theory of X-ray diffraction. $(\Delta d/d)_{strain}$ corresponds to the lattice-parameter variation caused by the internal strain. w_d is the divergence of the incident beam (FWHM).

For perfect crystals $(\Delta d/d)_{strain}$ and w_s are zero and the dynamical rocking curve is one or more orders of magnitude smaller than the beam divergence used in X-ray diffraction configurations, *i.e.* the intersection of the w-θ_B curve with the ordinate ($\theta_B = 0°$) represents the maximum value of the beam divergence. In the case of imperfect crystals the distribution function for the mosaicity is unknown and therefore the deconvolution cannot be done exactly. Only a raw value of the mosaic spread can be given.

Results

The measurements were carried out with the five-circle diffractometer (Kupcik, Wulf, Wendschuh, Wolf & Paehler, 1983) at HASYLAB (DESY, Hamburg). The operating parameters of the storage ring DORIS II were 3·7 GeV and 60–20 mA. The X-ray beam was monochromatized to $\lambda = 0{\cdot}917\ (1)$ Å by a flat Ge (111) double monochromator. In order to reduce the influence of polarization on the diffracted intensities the diffraction plane was oriented vertically with respect to the electron orbit in the storage ring. The spherical CaF_2 crystal 90 μm in diameter is the one used in previous experiments (Bachmann, Kohler, Schulz & Weber 1985). The FWHM can be obtained directly from the step-scan profiles of the reflections measured in the ω or ω-2θ mode. No significant difference is found in the FWHM for either mode. The step width was usually 0·003°. In the case of very sharp peaks of the perfect silicon crystal the step width was reduced to 0·001°. Both A and B could be determined by a least-squares fit based on (3) to the experimental results.

It is remarkable that the strongest reflections 111 and 220 have a FWHM that is significantly greater than expected from the least-squares fit. This deviation is caused by extinction. The value $B = 5 \times 10^{-4}$ found in this fit is of the same order of magnitude as the theoretically expected wavelength range produced by the double monochromator. The extrapolation $\theta_B \to 0$ gives $A = 79''$ for the 90 μm CaF_2 crystal (Fig. 1).

A perfect silicon crystal with a polished (111) surface was used for the estimation of the beam divergence w_d. The reflection profiles of the symmetrical Bragg reflections 111, 333, 444 and 555 were measured with a beam diameter of 0.1 mm. From the w-θ_B plot given in Fig. 2 it follows that $B = 4{\cdot}5 \times 10^{-4}$ and $A = 24''$ of arc. In order to simulate the influence of the crystal size the experiments with the perfect silicon crystal were carried out with different cross sections of the X-ray beam (0·1, 0·2, 0·5 and 1 mm in

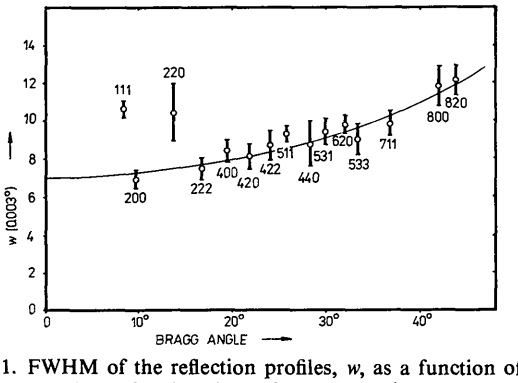

Fig. 1. FWHM of the reflection profiles, w, as a function of the Bragg angle θ_B for the 90 μm CaF_2 crystal (synchrotron radiation, $\lambda = 0{\cdot}917$ Å). The error bars result from the averaging among symmetrically equivalent reflections.

diameter). These measurements were done while DORIS II operated at 5·27 GeV and 25–12 mA. The double monochromator was also set to $\lambda = 0{\cdot}917$ Å, but the misadjustment of the second crystal was varied as compared to the experiment at 3·7 GeV in order to suppress higher harmonics. Fig. 3 summarizes the dependence of A on the diameter of the X-ray beam. The divergence of the synchrotron radiation given by Beimgraben, Graeff, Hahn, Knabe, Koch, Kunz, Materlik, Saile, Schmidt, Sonntag, Sprüssel, Weiner & Zietz (1981) is in good agreement with the value of A extrapolated to beam diameter zero.

Discussion

Beam divergence w_d and mosaic spread w_s can only be separated to a limited degree since the distribution functions are unknown and the deconvolution can therefore not be carried out exactly. In the case that both contributions are of the same order of magnitude the mosaic spread can be approximated by

$$w_s = (A^2 - w_d^2)^{1/2}. \quad (5)$$

The mosaic spread of the 90 μm CaF_2 crystal then amounts to 75″. If a Gaussian distribution is assumed one obtains $g = 0{\cdot}9 \times 10^3$ by means of (2).

In structure investigations with a conventional X-ray tube and crystal monochromator the information on the mosaic spread is hidden by the beam divergence, which lies in the range from 5 to 10′. In this case a separation of the two contributions is hardly feasible.

Concerning its applicability, the method described must be limited to experimental situations in which not all reflections are affected by extinction. Otherwise the analysis of the w–θ_B plot is not possible. Such an example is shown in Fig. 4. These are results from the same 90 μm CaF_2 crystal as used in the first experiment, but with the wavelength of the synchrotron radiation changed to 1·714 Å. No unique dependence of w on θ_B can be discerned. On the other hand, Fig. 5 shows results of a previous investigation of a 6 μm CaF_2 crystal with synchrotron radiation at the wavelength $\lambda = 0{\cdot}91$ Å (Bachmann, Kohler, Schulz & Weber, 1985). In contrast to the experiments discussed above, the diffraction plane was parallel to the plane of the electron orbit in the storage ring. This leads to low intensities for Bragg angles near 45° because of the polarization of the radiation. In the analysis of the FWHM no problems arise as long as the reflection profiles can be measured with good counting statistics. It can clearly be seen in Fig. 5 that the influence of extinction is very low. Also, the strongest reflections are in good agreement with (3). Unfortunately, the beam divergence was not estimated by an experiment with a perfect single

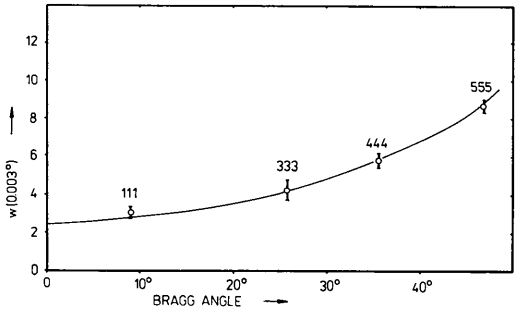

Fig. 2. Plot of w against θ_B for a perfect silicon crystal (λ = 0·917 Å, beam diameter 0·1 mm).

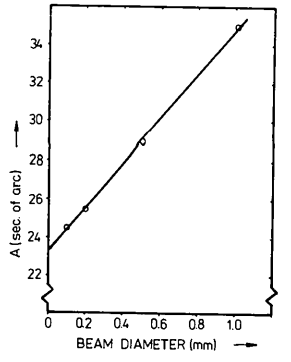

Fig. 3. FWHM of the reflection profiles of the perfect silicon crystal extrapolated to $\theta_B = 0$ [this corresponds to A in (3)] as a function of the diameter of the incident synchrotron X-ray beam (λ = 0·917 Å).

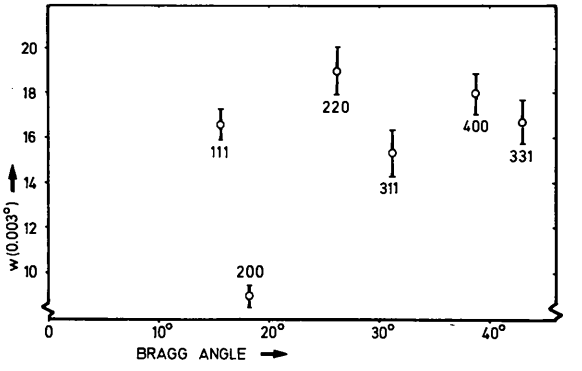

Fig. 4. Plot of w against θ_B for the 90 μm CaF_2 crystal at λ = 1·714 Å. Owing to strong extinction no unique function can be derived.

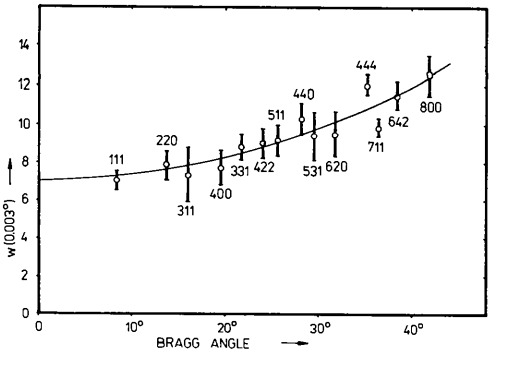

Fig. 5. Plot of w against θ_B for the 6 μm CaF_2 crystal ($\lambda = 0{\cdot}91$ Å).

crystal. The least-squares fit gives $B=6\times10^{-4}$ and $A=77''$. It can be concluded that the mosaic spread of the 6 μm crystal is of the order of 70″, but the reflection profiles are often divided into separate peaks. So the assumption of an analytical distribution function is only a rough approximation. This can also be seen in the correlation coefficient r of the fit based on (3). The function $w=a+b\tan\theta_B$ gives a better r value, but this relation is outside the usually accepted treatment. The estimated value of w_s especially in the case of the small crystal should be seen as the maximum value.

In general, the extinction parameter g is dependent on the crystal orientation (Coppens & Hamilton, 1970). This anisotropy can be revealed by a corresponding analysis of the FWHM. The variation in the FWHM of different but symmetrically equivalent reflections is the origin of the relatively large error bars in the figures.

Extinction correction

The Bragg intensities measured on the 90 μm CaF_2 sphere were used for structure refinements including secondary extinction of type I (Bachmann *et al.*, 1983). The refinements resulted in a mosaic spread of 28″ for 0·91 Å synchrotron radiation and 40″ for Mo $K\alpha$ radiation. These values deviate significantly from each other if a standard deviation of 5″ is assumed. They are in disagreement with the experimentally determined mosaic spread of 75(3)″. The reason for the differences between these three values lies most probably in the way the extinction was corrected in the structure refinements. The correction factor Y for an individual intensity measurement is applied in the form

$$I_c = I_m / Y \qquad (6)$$

with I_c and I_m the corrected and measured intensities respectively. Y values for both primary and secondary extinction are calculated in the form (Becker & Coppens, 1974)

$$Y=\{1+ax+A(\theta)x^2/[1+B(\theta)x^2]\}^{-1/2}. \qquad (7)$$

The coefficients a, $A(\theta)$, $B(\theta)$ are different for primary and secondary extinction. However, their θ dependence is similar. Therefore, extinction effects can usually be corrected by refining only secondary extinction, which absorbs in this way the influence of the primary extinction. The calculated mosaic spread is too small in such cases. Furthermore, the mosaic spreads calculated from intensity measurements at two wavelengths differ from each other. This is the situation found in our refinements and experiments. Therefore, we may assume that our intensity measurements are influenced by both primary and secondary extinction.

To check this hypothesis we carried out additional structure refinements with the intensity data of the 90 μm CaF_2 sphere, which were used by Bachmann, Kohler, Schulz & Weber (1985). The intensity data were corrected for primary extinction by (7) for radii ranging from $R=1$ to $R=6$ μm. These corrected intensities were then used for structure refinements including secondary extinction for type I in the same way as in Bachmann *et al.* (1985). Structure parameters and R values did not change significantly compared to those of Bachmann *et al.* (1985), except for the refined mosaic spread. Fig. 6 displays these combinations of domain sizes and mosaic spreads for the synchrotron radiation and the Mo $K\alpha$ radiation. To the measured mosaic spread of 75″ belongs a domain radius of $R=3$ and 5 μm for the Mo $K\alpha$ radiation and the synchrotron radiation ($\lambda=0{\cdot}91$ Å), respectively. The average of $R=4$ μm is reasonable for a crystal with rather high perfection. We have now a unique view of the crystal perfection of the 90 μm CaF_2 sphere. It is composed of crystallites with about 4 μm radius, which have a mosaic spread of 75″.

These values make it very probable that the intensities measured with the 6 μm crystal can be considered as free of extinction effects. As shown above, it has a mosaic spread of approximately 70″. Therefore, secondary extinction can be neglected. The same must hold for the primary extinction: The crystallites have to be considerably smaller than 4 μm in radius, otherwise we could not observe the typical diffraction profile of a distribution function. [A typical reflection profile of the 6 μm crystal is shown by Bachmann *et al.* (1983).] It follows that the crystallites probably have sizes smaller than the extinction lengths. The reason for the reduction of the domain sizes lies in the relative increase of the surface region for the 6 μm crystal compared to the 90 μm sphere.

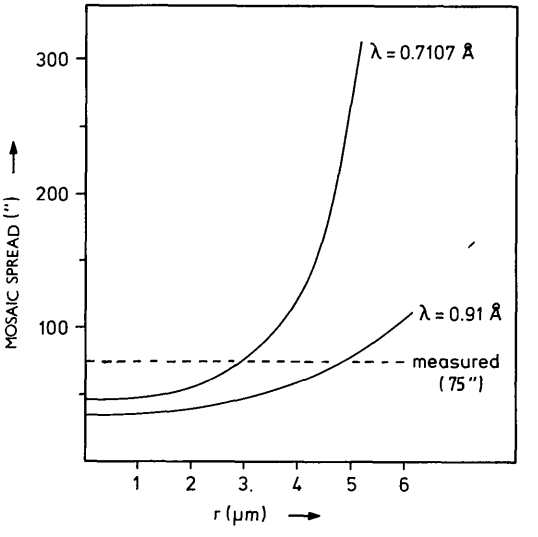

Fig. 6. Dependence of the refined mosaic spread on the applied correction for primary extinction for the 90 μm CaF_2 crystal.

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A Toolkit for Computational Molecular Biology. II. On the Optimal Superposition of Two Sets of Coordinates

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Abstract

The determination of the optimal transformation to superpose two sets of points has many applications to the analysis of structures of proteins and nucleic acids. A new formulation of this problem is presented, which reduces it to the unconstrained maximization of a function of a single variable. This method is currently being applied in investigations of common substructures of proteins.

1. Introduction

The superposition of two coordinate sets is the basis of a number of techniques for the analysis and comparison of molecular structures. Considerable effort has been made to develop fast algorithms (McLachlan, 1972; Diamond, 1976; Kabsch, 1976, 1978; McLachlan, 1979, 1982; Mackay, 1984; Ken-Knight, 1984).

Several efficient algorithms are known, and programs based on them are already fast enough for calculations in which only a few superpositions are required. However, in searching two or more protein structures for common substructures, a very large number of superpositions are required to test all combinations of segments from each pair of structures. Such analyses can sometimes be organized to superpose a succession of related substructures, so that the optimal transformation determined for one superposition may be nearly optimal for the next. In this case, optimization methods make it convenient to apply the results of one calculation to speed up the next. The method described here, a development of those used by McLachlan (1972, 1982), has this feature.

2. Statement of the problem

This section follows McLachlan's analysis very closely (McLachlan, 1972; *cf.* Golub & Van Loan, 1983). Let $\mathbf{x}_i$, $i = 1, \ldots, N$, and $\mathbf{y}_i$, $i = 1, \ldots, N$, be two sets of points in 3-space. We wish to superpose them by means of a rigid-body motion of the $\mathbf{y}_i$ into the set $\mathbf{y}'_i$ such that the sum of the squares of deviations

$$D = \sum_{i=1}^{N} (\mathbf{x}_i - \mathbf{y}'_i)^2$$

is minimized. Any rigid-body motion in 3-space may be decomposed into a rotation and a translation. The optimal translation is that which brings the mean positions (colloquially, 'centers of gravity') of the two sets into coincidence. We therefore may assume without loss of generality that the mean positions of the two sets of points coincide at the origin. The problem is to determine the proper rotation matrix

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