where
\[ w_i = 1/\sigma_i^2(y_i). \]

The averaged value \( \bar{y} \) estimates the mean, and \( \sigma_{\text{int}} \) and \( \sigma_{\text{ext}} \) estimate the standard deviation of the distribution sampled by the \( y_i \) values; \( \sigma_{\text{int}} \) is based on the internal consistency among the \( y_i \), and \( \sigma_{\text{ext}} \) is based on the external experimental error estimates \( \sigma(y_i) \), which are obtained by propagation-of-error calculations based on counting statistics, instrumental uncertainties and data reduction parameters.

Various more or less arbitrary actions are usually taken to deal with outlier values among the \( y_i \). Sometimes measurements that are more than, say, 5% or two or three estimated standard deviations from the estimated mean are rejected. Sometimes the median is accepted as the best estimate of the true mean. Sometimes the high and low values in a group of \( n \) measurements are rejected and the central \( n - 2 \) measurements are averaged. In the frequent cases of only two or three measurements, however, it becomes difficult or impossible to apply any criteria for rejection of discordant data.

We have adopted the following scheme to deal with outliers without outright rejection of any data. Accepting \( \mu = \bar{y} \) and \( \sigma = \max(\sigma_{\text{int}}, \sigma_{\text{ext}}) \), we calculate relative normal probabilities,
\[ p_i = \exp[-(y_i - \mu)^2/(2\sigma^2)], \]
for each of the \( n \) measurements. We then re-evaluate \( \bar{y}, \sigma_{\text{int}} \) and \( \sigma_{\text{ext}} \) using the above formulas but with \( w_i \) replaced by the product \( p_i w_i \). In practice, we take the new \( \mu \) and \( \sigma \) corresponding to the revised values and repeat the cycle once to refine the values of \( \bar{y}, \sigma_{\text{int}} \) and \( \sigma_{\text{ext}} \). The ratios \( \sigma_{\text{int}}/\sigma_{\text{ext}} \) are used in a bivariate analysis of variance against \( |F|^2 \) magnitude and \( (\sin \theta)/2 \). This, in turn, allows improved estimates of the standard deviations and least-squares weights, even for the reflections measured only once. Normal probability weighting has been incorporated as an optional alternative to discordant data rejection in our data reduction programs (Blessing, 1986, 1987).

We are grateful for the support of our research by USDHHS PHS NIH grants Nos. GM34073 and DK19856 (RHB) and HL32303 (DAL).

References


An experimental test of an elastically bent silicon crystal as a thermal-neutron monochromator.

By P. Mikula, P. Lukáš and R. Michalec, Nuclear Physics Institute, Czechoslovak Academy of Sciences, 250 68 Řež near Prague, Czechoslovakia

(Received 3 March 1987; accepted 13 May 1987)

Abstract

The effectiveness of employing an elastically bent perfect Si (111) crystal as a monochromator for neutron-diffraction experiments is demonstrated on rocking curves presented for a flat perfect Si (220) crystal and a mosaic Fe (110) crystal, for two different collimations of the incident beam. For the sake of comparison equivalent rocking curves with a conventional mosaic Zn monochromator are also introduced. The experimental results obtained indicate that curved perfect-crystal monochromators may become a useful alternative to mosaic-crystal ones.

In a previous paper (Mikula, Kulda, Horalik, Chalupa & Lukáš, 1986; paper I) we proposed a new type of highly efficient thermal-neutron monochromator based on an elastically bent perfect Si crystal in a strongly asymmetric diffraction geometry and presented some of its diffraction properties. In this short paper we present rocking curves of perfect Si and mosaic Fe crystals in the monochromatic beam obtained experimentally from the proposed monochromator as well as from a conventional mosaic Zn one.

Following the proposal introduced in paper I we used in our experiment the fully asymmetric diffraction geometry as displayed schematically in Fig. 1. It is clear that the width of the output monochromatic beam just behind the crystal is equal to the thickness of the crystal. For a sufficiently thick crystal the flux of the monochromatic neutrons is independent of the crystal thickness, but dependent on the bending radius \( R \) and the width of the incident polychromatic beam \( W_i \).

In paper I the integrated reflectivity, \( \rho_0^P \), of the whole irradiated crystal volume per unit cross section of the output beam is given by
\[ \rho_0^P = \delta_0 \theta(R) r(R) A(\mu), \quad (1) \]
where \( \delta_0 \theta(R) = |x_2 - x_1|/R \) is the total change in the Bragg angle for the diffracted beam on its path through the crystal between the points \( x_1 \) and \( x_2 \), \( r(R) \) is the peak reflectivity, equal to \( |1 - \exp(-Q R)| \) in the asymmetric geometry (Kulda, 1984) and
\[ A(\mu) = |x_2 - x_1|^{-1} \int_{x_1}^{x_2} \exp(-\mu x) \, dx \]
is the attenuation factor. Here \( \mu \) is the linear attenuation coefficient and \( Q = F_{\text{hl}}^2 \lambda^2/\phi_0^2 \sin 2\theta \), where \( F_{\text{hl}} \), \( \theta \) and \( \phi_0 \) are...
the structure factor, the neutron wavelength and the unit-cell volume, respectively.

The comparison was made at \( \lambda = 0.2 \text{ nm} \) with the 111 reflection of an elastically bent Si monochromator and the 002 reflection of a Zn mosaic monochromator which had a full width at half maximum (FWHM) of the mosaic distribution of about 17' and a peak reflectivity \( r(\Delta \theta = 0) = 0.4 \). In both cases we used the same width of 4 mm and height of 20 mm of the output monochromatic beam. Moreover, in this case the width of the incident beam and the bending radius were \( W_1 = 3 \text{ cm} \) and \( R = 28 \text{ m} \), respectively. The dimensions of the Si crystal bar were \( 140 \times 30 \times 5 \text{ mm} \) (length \( \times \) height \( \times \) thickness). Taking into account the collimation of the incident beam and the value of the scattering angle \( 2\theta \), we find that the maximum length of the irradiated crystal volume was about 5.3 cm. Then we can easily calculate the effective mosaicity \( \delta\phi(R) = 6.5' \), \( r(R) \approx 1 \) and \( \Lambda(\mu) = 0.9 \). Finally, we obtain the value of the total integrated reflectivity per unit cross section of the output beam, \( \rho_0 = 5.9' \).

Figs. 2(a)–(d) display the rocking curves corresponding to the perfect flat Si (220) crystal and to the mosaic Fe (110) crystal used with the bent Si (111) and the mosaic Zn (002) monochromator. The FWHM of the mosaic distribution of the Fe crystal was about 2'. The comparison was made for two different collimations \( \Delta x \) of the incident beam. Inspection of Figs. 2(a)–(d) reveals that the values of the FWHM corresponding to the rocking curves with the bent Si monochromator are about 10% smaller than that corresponding to the Zn monochromator. As the peak intensities in both cases are practically the same, we can state that for \( R \) less than 30 m the bent Si monochromator is equivalent to or even better than the mosaic Zn one. But, in practice, the Si crystal bar could be bent to a still smaller radius of curvature \( R \). Furthermore, sometimes the experimental conditions permit the use of a larger width \( W_1 \) of the incident beam. Thus, for work at fixed wavelengths, one could achieve a considerable gain in the flux of monochromatic neutrons as well as in the intensity diffracted by a sample using the joint effect of the enlarged 'effective mosaicity' \( \delta\phi(R) \). The increase of \( \delta\phi(R) \) need not always be accompanied by a loss in resolution because, for example for a point sample, the use of the monochromator with a tunable radius of curvature allows one to adapt the experimental conditions so that focusing in reciprocal space may be achieved (Scherm, Dolling, Ritter, Schedler, Teuchert & Wagner, 1977; Popovici & Stoica, 1983; Arrott & Templeton, 1985). In reality, however, there are many other contributions, e.g. finite size of the sample or the thickness of the crystal, which all influence the final resolution. In the

Fig. 1. Schematic sketch of diffraction by a bent single crystal in special asymmetric geometry as a neutron monochromator.

Fig. 2. Rocking curves (a), (b) of a perfect flat Si (220) crystal and (c), (d) of a mosaic Fe (110) crystal in the beam monochromatized by a bent Si (111) and a mosaic Zn (002) monochromator for two different collimations \( \Delta x \) of the incident beam.
course of our test experiments we changed the radius of
curvature from \( R = 60 \) down to \( R = 20 \) m. The FWHM of
the rocking curves varied in all cases within 10%.

References


Computer Programs


**Diffraction peak shapes: a profile refinement method for badly resolved powder diagrams.** By VINH TRAN
and ALAIN BULEON, Laboratoire de Physicochimie des Macromolécules, Institut National de la Recherche Agronomique,
Centre de Recherches de Nantes, Rue de la Géraudière, 44072 Nantes CEDEX, France

(Received 7 October 1986; accepted 23 January 1987)

**Abstract**
A program has been specially written for biological powder spectra. Most existing programs are not suitable for such poorly resolved diagrams with broad bands in which individual peaks are not well separated. A more efficient version of the COMPLEX algorithm is used and this direct optimization method reduces the risk of false minima. Numerous internal parameters and options in the optimization algorithm as well as in the profile calculations lead to great flexibility. The performance and the limits of this version are tested by two applications on \( \alpha \)-lactose monohydrate and native cellulose partial spectra. In the first case the results are excellent, according to values in the literature, and in the second case this program indicates some interesting features. This powerful algorithm can be used for more complicated refinements.

**I. Introduction**
X-ray diffraction patterns from biological fibrous or powdered polymers are generally characterized by a relatively small number of broad overlapping peaks often superposed on a diffuse halo. These features prevent an accurate determination of diffraction-line intensities and of unit-cell parameters. Many sophisticated calculations have been reported in the literature including deconvolution procedures (Louboutin & Louër, 1972; Taupin, 1973; Huang & Parrish, 1975; Moraweck, de Montgolfier & Renouprez, 1977; Law & Hogan, 1984), Rietveld refinements (Rietveld, 1969; Pham, Choisnet & Raveau, 1975; Malmros & Thomas, 1977; Young, Mackie & Von Dreele, 1977; Sakata & Cooper, 1979; Hewat & Sabine, 1981; Cooper, 1982; Thompson & Wood, 1983; Ahtee, Unonius, Nurmelu & Suortti, 1984) or classical fitting methods (Rietveld, 1967; Mortier & Coste noble, 1973; Sonneveld & Visser, 1975; Hall, Veeraraghavan, Rubin & Winchell, 1977; Langford, 1978; Suortti, Ahtee & Unonius, 1979; Brown & Edmonds, 1980; Prince, 1981; Naidu & Houska, 1982; Toraya, Yoshimura & Sōmiya, 1983). The first two methods are not easily available for powder patterns of polysaccharides because of their para-crystallinity and typical features such as preferred orientations, granularity or hydration effects. This is related to the lack of precise knowledge about the mathematical description of both peaks and background as shown by the numerous existing models summarized by Young & Wiles (1982). The noisy outline of diffraction lines prevents the safe use of optimization methods such as least-squares adjustments or other derivation procedures, since they often lead to false optima.

In the present paper, a method is given to calculate, from Debye–Scherrer powder X-ray diffraction diagrams, the position and the relative intensities of different peaks with or without unit-cell constraints. The proposed computer program includes a new version of the COMPLEX method (Box, 1965, 1966) for optimization with a profile-fitting technique using a Pearson VII function optionally connected to a classical unit-cell-parameters refinement. This method has been successfully applied to materials with relatively well defined structures such as \( \alpha \)-lactose monohydrate and native cellulose before being used to determine unit-cell parameters and relative intensities for more complicated substrates. This method yields some directly available structural data (e.g. unit-cell parameters, intensities) for subsequent calculations, but it is less powerful than the Rietveld method which leads to the determination of atomic positions. Nevertheless, it can be more easily applied to polysaccharide diffraction diagrams preceding the usual calculations for atomic positions and molecular packing with classical conformational-analysis programs.

Only major experimental corrections such as Lorentz–polarization and angle-dependent features are taken into account.

0021-8898/87/050430-07$1.50 © 1987 International Union of Crystallography