A Medium-Resolution Double-Crystal Diffractometer for the Study of Small-Angle Neutron Scattering

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Abstract

The angular resolution of the parallel (1, -1) double-crystal setting has been relaxed from the original value of 10 μrad for perfect silicon crystals into the region 0.1-1 mrad by their elastic deformation. The totally reflecting region of the dynamical diffraction curve is broadened proportionally to the deformation while the wings as well as the diffuse scattering intensity are not affected substantially. This experimentally verified fact causes gain both in intensity and the signal/noise ratio. First experiments were performed with bent Si single-crystal bars in symmetric 220 reflection geometry at 0B = 16°7' with bending radii of the order of 100 m, angular resolution 0-6 mrad and an effective neutron flux at the sample position of 400 mm-2 s-1 were achieved. These values do not depend on beam cross section.

1. Introduction

Contemporary small-angle neutron scattering (SANS) instruments equipped with large-area position-sensitive detectors are a widely used tool for investigations of inhomogeneities in materials as well as studies of various biological objects. The range of real-space dimensions of such objects accessible at most instruments has an upper limit of 100 nm corresponding to a maximum scattering vector resolution slightly below 0.1 nm-1. Above this limit the classical SAS machines, with a few exceptions such as the D11 at ILL, Grenoble, for both X-rays and neutrons (Schneider & Shull, 1971; Shil'stein, Somenkov & Kalanov, 1976; Schielbe, Schmidt, Schild & Eichhorn, 1981). In a few cases mosaic crystals were employed (Mook, 1974) to enhance the luminosity. This solution is, however, applicable to the study of effects with high SANS cross sections only, the limiting factor being the high background level caused by long tails of the mosaic-spread distribution curves and by diffuse scattering. The use of asymmetrically cut perfect crystals does not bring much improvement as the higher angular acceptance is paid by a decrease of the useful cross section of the primary beam.

The aim of this paper is to report another way of obtaining a higher luminosity through the employment of elastically deformed crystals. It is a well

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<th>Table 1. Dynamical scattering of X-rays and neutrons of wavelength ( \lambda = 0.154 ) nm on silicon (Pinsker, 1978)</th>
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established fact that the totally reflecting region of the dynamical rocking curve is broadened proportionally to the deformation while its tails are not affected substantially (Klar & Rustichelli, 1973). Thus a gain in the neutron flux at the sample position, an enhanced signal/noise ratio and the possibility of a continuous adjustment of the angular resolution may be expected as the major advantages in comparison to the asymmetrically cut or mosaic single crystals.

2. Theoretical background

The intensity diffracted by a parallel (1, -1) double-crystal arrangement for a given angular position $\theta$ of the second crystal may be expressed as (e.g. Pinsker, 1978)

$$I(\theta) = I_0 A \int_{-\infty}^{+\infty} \phi_1(\xi) \phi_2(\theta - \xi) \, d\xi$$

$$= I_0 A f_0(\theta).$$

(1)

Here $\phi_1$ and $\phi_2$ denote the rocking curves of the first and second crystal, respectively, $\xi$ and $\theta$ are the corresponding angular variables, measured in the plane of incidence (assumed to be horizontal) which are zero at the precise reflecting position. $I_0$ represents the incident flux and $A$ is a product of the normalization constants that ensure that

$$\int_{-\infty}^{+\infty} \phi_i(\xi) \, d\xi = 1$$

for $i = 1, 2$.

A small-angle scattering specimen placed between the crystals will deflect the neutrons both in the horizontal and vertical directions by angles $\eta_h$ and $\eta_v$, respectively. The probability for such events is given by the macroscopic differential cross section.

$$\frac{d\Sigma}{d\Omega} = h(\eta_h, \eta_v).$$

The parallel (1, -1) double-crystal setting is very insensitive to angular deviations of the neutron beam perpendicular to the plane of incidence, the only limitation being the opposite curvature of the Kossel circles. For a rocking-curve width $w$ and a Bragg angle $\Theta_B$ the vertical width is

$$w_v = 2(2w \cos \Theta_B)^{1/2}.$$

For $w = 25^\circ$ and $\Theta_B = 16^\circ - 7^\circ$ one obtains $w_v = 0.03 \text{ rad} = 1.72^\circ$. Therefore, at an arbitrary position of the second crystal the SANS differential cross section is integrated over the vertical component of the scattering angle and only

$$g(\eta_v) = \int_{-w_v/2}^{+w_v/2} h(\eta_h, \eta_v) \, d\eta_v$$

(2)

is measured. Therefore, the SANS cross-section measurement is performed in the long-slit geometry (Guinier & Fournet, 1955). The effective slit height is obviously limited only by $w_v$ of the second crystal and by the vertical collimation between sample and detector. In many practical cases one can use the approximation $h(\eta_v, \pm w_v/2) = 0$, which corresponds to the measurement performed in the infinite slit geometry. In what follows we will set

$$c = \int_{-\infty}^{+\infty} g(\eta) \, d\eta \quad \text{and} \quad g(\eta) = 1 \cdot c g(\eta).$$

The intensity of the beam reflected by the second crystal may be expressed by a formula similar to (1):

$$I_s(\theta) = I_0 A B f_s(\theta),$$

(3)

where the transmission coefficient $B$ takes into account intensity losses due to absorption and scattering to large angles by the sample. The beam is now formed by a superposition of the SANS contribution smeared by the double-crystal rocking curve $f_0$,

$$I_0 A B c \int_{-\infty}^{+\infty} \phi_1(\xi) \, \bar{g}(\eta - \xi) \phi_2(\theta - \xi) \, d\xi \, d\eta,$$

(3')

and the undeflected part,

$$I_0 A B (1 - c) \int_{-\infty}^{+\infty} \phi_1(\xi) \phi_2(\theta - \xi) \, d\xi.$$

(3'')

Combining (3) with (3') and (3'') we arrive at an expression for $f_s$:

$$f_s(\theta) = (1 - c) f_0(\theta) + c f_0 \cdot \bar{g}(\theta).$$

(4)

The functions $f_0(\theta)$ and $\bar{g}(\theta)$ are normalized to unit integrals, hence also

$$\int_{-\infty}^{+\infty} f_s(\theta) \, d\theta = 1.$$
some suitable extrapolation. For the sake of simplicity in the following considerations we shall set $G(\theta) = G(\theta_{\text{min}})$ for $|\theta| \leq \theta_{\text{min}}$ for practical purposes, however, the Guinier law $a \exp(-b\theta^2)$ (Guinier & Fournet, 1955) or some other more sophisticated extrapolation should be preferred to obtain a more accurate estimate of $G(\theta)$.

The instrumental function $f_0(\theta)$ may be non-negligible in the whole range of $\theta$ values when a double-crystal diffractometer is used. In this case, for an exact decomposition of $f_s(\theta)$ into the terms on the right-hand side of (4) the knowledge of the cross-section value $c$ would be required. On the other hand, $c$ can be determined only as

$$c = \int_{-\infty}^{+\infty} G(\theta) \, d\theta.$$  

A simple iterative procedure based on this consideration is proposed to solve this problem. Let us estimate $c$ as

$$c^{(0)} = 2 \left[ f_s(\theta_{\text{min}}) \theta_{\text{min}} + \frac{\theta_{\text{max}}}{\theta_{\text{min}}} \int_{\theta_{\text{min}}}^{\theta_{\text{max}}} f_s(\theta) \, d\theta \right].$$  

It is clear that $c^{(0)} > c$ as $f_s(\theta)$ also includes the remainder of $f_0(\theta)$. With the help of $c^{(0)}$ an approximation $G^{(0)}(\theta)$ of $G(\theta)$ is computed

$$G^{(0)}(\theta) = f_s(\theta) - (1 - c^{(0)}) f_0(\theta),$$  

which satisfies $f_s(\theta) \geq G^{(0)}(\theta)$ for all $\theta$. This procedure may be repeated using the approximation $G^{(0)}(\theta)$ to determine $c^{(i+1)}$. For well behaved data a monotonous succession of the values $c^{(i)}$ results, converging to $c$. The whole process is terminated as soon as the change of $c^{(i)}$ is less than the expected experimental error. Instabilities (oscillations in the sequence) may occur whenever the SANS intensity is of the order of the background level fluctuations.

The resulting function $G^{(0)}(\theta)$ is a slit-smeared SANS curve similar to those obtained in the X-ray instruments (e.g. Kratky camera). Standard numerical procedures, involving either deconvolution or direct fitting have to be employed to extract the information about the particular scattering object.

### 3. Diffraction by bent crystals

A considerable amount of work on the diffraction of neutrons on large-scale-elastically-deformed single crystals has been done in the past decade. Our considerations will be based on the treatment developed in the works of Klar & Rustichelli (1973); Albertini, Boeuf, Mazkedian, Melone, Rozzi & Rustichelli (1977) and Michalec, Mikula & Vávra (1977). Their theory applies to all cases when crystal regions of dimensions of the extinction length may be considered as perfect. The diffraction properties of such crystals are then similar to those of a pack of perfect crystalline lamellae mutually misoriented by just the width of the Darwin rocking curve. In cases when the change of the local departure from the Bragg angle $\Delta \Theta(r) = \Theta(r) - \Theta_{\text{B}}$ along the beam path $(r_1, r_2)$ is monotonous, the width of the total reflection range is approximately equal to

$$\delta \Theta = |\Delta \Theta(r_1) - \Delta \Theta(r_2)|.$$  

Let us consider a simple case of the symmetric Bragg reflection by a single-crystal plate of length $L$ and thickness $T$ homogeneously bent with a radius $R$. For the coordinate system chosen in Fig. 1 we can write for the local displacement $u(x)$ on the central line to a good approximation

$$u(x) = u_0 + \frac{x^2}{2R}.$$  

The variation of the interplanar spacing $d_{\text{hl}}$ over the crystal thickness can be estimated with the help of the elementary theory of elasticity to be less than $T/6R = 8 \times 10^{-6}$ for $R = 100 \text{ m}$ and $T = 5 \text{ mm}$. This corresponds to an angular deviation $\Delta \Theta' = 0.5^\circ$ in the Bragg equation for $\Theta_{\text{B}} = 16.7^\circ$, a value less than the angular width of the Darwin curve (see Table 1). The prevailing influence on the diffraction by a bent crystal is exhibited by the local angular deviations of the lattice planes

$$\Delta \Theta''(x) = \tan[\Delta \Theta''(x)] = \frac{du(x)}{dx} = \frac{x}{R}.$$  

In the following considerations an effective value $\Delta \Theta(x) = \Delta \Theta''(x)$, constant over the crystal thickness, is assumed.

The bent-crystal rocking curve may be to a good approximation represented by a rectangle. Its width

![Fig. 1. A schematic sketch of the bending device (a) and the diffractometer set-up (b): 1.2 crystals bent in the same sense at different radii $R_1, R_2$; 3 polyethylene shielding; 4 Cd slits; 5 sample.](image-url)
δθ for a narrow incident beam in the symmetric Bragg case in accordance with (7) and (9) is

$$\delta \theta = (T/R) \cot \Theta_B.$$  \hfill (10)

The height is given by the reflectivity formula for a deformed crystal (Kulda, 1983) by

$$r = 1 - \exp(-R/\rho),$$  \hfill (11)

where

$$\rho = \Omega^2 \cos^2 \Theta_B/(4 F_{hk}^2 d_{hk}^2)$$  \hfill (12)

is a characteristic value of the bending radius dependent on the structure factor $F_{hk}$, elementary cell volume $\Omega$, interplanar spacing $d_{hk}$ and Bragg angle $\Theta_B$. The exponential term in (11) predicts a drop in reflectivity and saturation of the integrated intensity at higher deformations.

In a double-crystal arrangement for a successive reflection of a neutron passing the points $x_1$, $x_2$ in the first and second crystal, respectively, it is necessary that the corresponding scattering angles coincide, $\Theta(x_1) = \Theta(x_2)$. Simultaneously, $\Theta(x_2)$ is the sum of the take-off angle after the first reflection $\Theta_B + 2\Delta \Theta(x_1)$ and the local deviation $\Delta \Theta(x_2)$. Hence the condition reads $\Delta \Theta(x_1) = -\Delta \Theta(x_2)$ and, together with the fact that the scattering vectors are antiparallel, it implies that both crystals have to be bent in the same sense (see Fig. 1b) at the same radii $R_1 = R_2$. This is, however, true only in the absence of beam divergence, when all neutrons reflected at a point $x_1$ of the first crystal will pass through a point $x_2$ (or a small area) of the second crystal.

In a real experimental arrangement with a beam divergence of about 20', crystals spaced by 1–2 m and at low scattering angles, the situation is somewhat different. A point at the second crystal receives neutrons scattered within an interval of several centimetres along the first crystal. The condition of equal scattering angles cannot then be fulfilled for all neutrons simultaneously. In general, it is convenient to cover a greater angular range $\Delta \theta_2$ along the path of the beam through the central part of the second crystal by choosing a smaller bending radius, $R_2 < R_1$. The variation of the deviation $\Delta \Theta(x_2)$ along the second crystal becomes steeper in this way and $\Delta \Theta$ according to (9) will be too large in the edge parts of the irradiated area to satisfy the reflection condition for any neutron. Peak-intensity saturation for this reason has to be expected at smaller deformations than predicted by the product of the reflectivities calculated for both crystals from (11). Therefore, the best advice is to keep the distance between the crystals as short as possible.

4. Optimization experiments

In the first experiments a silicon 220 reflection was employed giving 0·11 nm neutron wavelength at $\Theta_B = 16\,^o$. Massive polyethylene shielding combined with a rectangular cadmium slit (Fig. 1b) defined the primary-beam cross section, 2 x 2 cm, a second Cd slit of the same aperture was placed between the crystals to prevent parasitic scattering at the sample holder. The crystals were plates of dimensions 200 x 30 x 5 mm mechanically bent with radii of the order 100–1000 m. The bending device, designed by Vrzal (1976), enables a continuous change of the bending radius in the range from 20 to 1800 m with direct measurement of the bending amplitude $u_0$ (see Fig. 1) by a contact micrometer.

At the beginning the first crystal was bent at various radii and rocking curves were taken with the second, nondeformed, crystal. The theoretical predictions concerning the form of the rocking curve (box-like shape with constant height and width proportional to 1/R) were verified for $R \geq 60$ m. Below this value the peak reflectivity drops in good agreement with (11) for $\rho = 14·3$ m computed from (12) for the actual values of the experimental parameters (for a detailed description of a similar experiment see Kulda, 1983).

As a second step, the rocking curves for numerous combinations of the bending radii $R_1$ and $R_2$ were measured to establish their optimum choice for a given angular width (Figs. 2a, b). For values of $R_2$ at a given $R_1$, the rocking curves have maximum peak intensity at $R_2 = R_1/3$ and at a slightly higher value, $R_2'$, the minimum width is achieved. The optimum choice of $R_2$ lies obviously in the interval $(R_2, R_2')$. Peak intensities and rocking-curve widths for optimum combinations of $R_1$ and $R_2$ are displayed in Fig. 3. Complete saturation of the peak-intensity dependence for $R_1 \leq 100$ m is observed while the losses determined from the product of peak reflectivities from (11) and (12) should not exceed 10%. The increased rate of saturation as well as the discrepancy between $R_2'$ and $R_2$ and the necessity to choose $R_2 \approx R_1/3$ is imposed by the beam divergence exceeding 20’ and the long distance between the crystals as discussed at the end of § 3.

A further important characteristic of a SANS instrument is the background-to-peak ratio, which establishes the lower limit of scattering cross sections that can be measured. From the theoretical results the ratio can be expected to improve by a factor proportional to $1/R_1$ in comparison to the double-crystal arrangement with two perfect crystals. Fig. 4 displays some values $F$ of the background-to-peak ratio, where the background is determined as the intensity at $2 \times$ FWHM distance from the peak of the double-crystal curve. Typical values of $F$ are $5 \times 10^{-4}$ and $2 \times 10^{-3}$ for the radii $R_1$ of 400 and 1600 m, respectively.

In the course of the SANS testing experiments the samples were mounted on a four-arm carousel holder placed between the crystals. At each angular position
of the second crystal counts from three different samples and from the empty holder were recorded successively. The curves measured with a sample between the crystals were normalized to give the same integral as those without the sample. The intensity losses due to absorption as well as to both coherent and incoherent scattering outside the measured range were eliminated in this way. In a further step the smeared SANS curve $G(\theta)$ was extracted from the measured data $f_s(\theta)$ and $f_d(\theta)$ by means of the above described iterative procedure. No effort has been made to extract specific SANS information from $G(\theta)$. However, routine desmearing or fitting procedures have to be applied at this point.

One of the first samples was a 0.8 mm thick Teflon foil investigated at an angular resolution $\Delta \theta = 0.4$ mrad; the raw data are displayed in Fig. 5. The measurement was continued at a higher resolution $\Delta \theta = 0.1$ mrad. Both SANS curves obtained in this way are plotted in Fig. 6 together with the X-ray data for the same sample, taken with a Kratky camera in long-slit geometry. All three curves agree well within a multiplicative factor because no absolute intensity calibration in the X-ray measurement was performed and samples of different thickness were used in the neutron case. The slopes at higher angles correspond in both cases to the $Q^{-3}$ dependence characteristic for

![Fig. 2](image1)

**Fig. 2.** Double-crystal reflection-curve widths $\Delta$ (FWHM) $(a)$ and peak intensities $(b)$ for various combinations of the bending radii $R_1$ and $R_2$. The $R_1$ values are given in metres.

![Fig. 3](image2)

**Fig. 3.** The dependence of the parameters (peak intensity and FWHM) of an optimized setting on the reciprocal value of the bending radius of the first crystal.

![Fig. 4](image3)

**Fig. 4.** The background-to-peak ratio determined from the double-crystal reflection curves $I(\theta)$ as $I(2\Delta)/I_M$, where $\Delta$ denotes the FWHM and $I_M = I(0)$ is the peak intensity.
the Porod range in long-slit geometry (Guinier & Fournet, 1955).

5. Discussion

Both the advantages and the drawbacks of the presented SANS instrument originate from the fact that crystals were employed instead of slit collimators. In this way the momentum resolution is decoupled from the beam cross section and may be increased without excessive losses in intensity. On the other hand, crystal reflection is far less efficient in beam handling than the transmission through slits where high values of contrast are achieved without great effort.

The peak intensity of the double-crystal rocking curves may be expected to approach the maximum value that can be obtained for a given angular resolution as long as the conditions for total reflection on both crystals are satisfied (bending radius \( R \geq 60 \text{ m} \)). The resulting effective flux at the sample position, \( 100-500 \text{ mm}^{-2} \text{s}^{-1} \), compares well with modest slit instruments. Further improvement is possible by reducing the distance between the crystals to decrease the influence of beam divergence in the successive reflection of neutrons on the bent crystals.

In comparison to other double-crystal diffractometers used until now for the SANS work, a great advantage is the shape of the rocking curve with its sharply cut-off tails. A background-to-peak ratio \( F = 5 \times 10^{-4} \) is already achieved at \( 2 \times \text{FWHM} \) from the peak position. With mosaic or perfect crystals, for the same ratio angular distances orders of magnitude greater would be required. On the other hand, a background level of \( 10^{-4} \times I_M \) is still high for many SANS applications as compared to the values below \( 10^{-8} \times I_M \) for slit instruments or Bonse–Hart diffractometers.

Another useful feature of the present instrument is the possibility of angular-resolution variation in the range \( 0.01-1 \text{ mrad} \) by adjustment of the bending radii of the crystals (Fig. 3). The time required for measurement of wide SANS curves may thus be reduced by splitting the whole angular range into intervals scanned at optimum resolution analogously to classical X-ray instruments with adjustable slit widths. In this way one of the major drawbacks – the necessity of step-by-step measurement – is somewhat compensated.

The \( Q \) range covered by this instrument partly overlaps with that of the slit instruments and extends to small \( Q \) values down to \( 0.001 \text{ nm}^{-1} \). Complementary experiments might be thus of some interest. One of their advantages would be the possibility of a straightforward determination of SANS cross sections on an absolute scale by the double-crystal instrument.

Until now our experiments have been performed on a conventional two-axis spectrometer with the silicon crystals available. Some restrictions were imposed by these facts, including the large distance between crystals (1.5 m) and the small Bragg angle 16.7°.
(limited by the first axis), which, together with the necessity to use the 220 reflection, resulted in the unfavourable wavelength of 0.11 m. For further experiments the use of a silicon 111 reflection at \(2\theta_B = 90^\circ\) is intended, which corresponds to a wavelength of 0.44 nm of neutrons from a Be filter. In this way a higher momentum resolution for a given angular resolution will be achieved and the cross section for double Bragg scattering in polycrystalline samples will be reduced substantially.

6. Conclusion

A flexible double-crystal SANS diffractometer was described. Its characteristic parameters are: effective neutron flux at the sample position 400 mm\(^{-2}\) s\(^{-1}\) (at \(\Delta Q = 0.003\) nm\(^{-1}\)), background-to-peak ratio of 2 \(\times 10^{-4}\), momentum resolution adjustable in the range from 0.5 to 10 pm\(^{-1}\) and covered momentum range from 0.001 to 0.1 nm\(^{-1}\). Normalization of the scattered intensity is performed directly on the incident flux so that the SANS cross sections are determined on an absolute scale.

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