Effect of crystal shape on neutron rocking curves of perfect single crystals designed for ultra-small-angle scattering experiments

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Abstract. The present study has been conducted in the framework of the channel-cut crystal design for the Kookaburra ultra-small-angle neutron scattering (USANS) instrument to be installed at the OPAL reactor of ANSTO. This facility is based on the classical Bonse-Hart method that uses two multiple-reflection crystal systems. The dynamical theory of diffraction by perfect crystals distinguishes two cases: the Darwin case applying to infinitely thick crystals and the Ewald solution for very small absorption taking into account the reflection from the rear face of a plane-parallel crystal reflecting in Bragg geometry. The former is preferable because it yields narrower rocking curves. To prevent the neutrons to “see” the rear face, grooves were machined into the backside of perfect Si test crystals for single reflection and filled with neutron absorbing material. These samples were examined at the S18 instrument of the Institut Laue-Langevin. Unexpectedly the crystals with empty slots showed an increase of the rocking curve width. When filling the slots with an absorber the widths decreased, but without reaching that of the Darwin curve. Understanding the results and achieving a successful crystal design call for the development of a theory that permits to describe neutron diffraction from crystals with a structured back face.

1. Introduction

The present study has been conducted in the framework of the channel-cut crystal design for the new ultra-small-angle neutron scattering (USANS) instrument named Kookaburra that is presently under commissioning at the ANSTO OPAL reactor [1]. This facility is based on the classical Bonse-Hart method [2] which consists of using two multiple-reflection crystal systems arranged in non-dispersive geometry to achieve a very steep decrease of the tails of the perfect crystal diffraction curves. This technique permits to detect very small angular deviations of the neutron beam after scattering from a sample placed between the two channel-cut crystals. The state-of-the art of this method and its performance have been reviewed recently by Agamalian et al. [3].

The diffraction process of X-rays and neutrons by perfect crystals is described by the dynamical theory. Two cases are distinguished:

- i) The Darwin solution for zero absorption that applies to infinitely thick crystals.
- ii) The Ewald solution for very small absorption that takes into account the influence of the rear face of a crystal reflecting in Bragg geometry.

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Because the former yields narrower rocking curves, for USANS experiments it is preferable to the latter. Several multiple reflection crystal schemes have been designed successfully to achieve the Darwin case [4,5]. However, they cannot be applied to the present instrument because of the big crystal size needed. Therefore we have been looking for a different crystal shape.

The idea we followed was to machine grooves into the backside of the channel-cut crystals and to fill them with neutron absorbing material such as cadmium or boron carbide powder. Indeed, this design prevents the neutrons to “see” the rear face of the crystal. Such crystals have been fabricated for single reflection and examined at the S18 instrument of the Institut Laue-Langevin, Grenoble, by recording rocking curves. Following a brief description of the Kookaburra layout, the details of the crystal design and the results will be given.

2. The USANS instrument Kookaburra at ANSTO

Figure 1 shows the principle of the Bonse-Hart small angle camera Kookaburra installed on a cold neutron guide at ANSTO’s Opal reactor. A detailed optimisation including the discussion of several scenarios has been carried out earlier [6].

![Figure 1. Principle of the USANS facility at ANSTO.](image)

The following design was chosen. A pyrolytic graphite doubly curved premonochromator set at a Bragg angle of 45° reflects simultaneously neutrons of wavelengths 4.74 Å and 2.37 Å from its (002) and (004) lattice planes, respectively.

![Figure 2. View of Kookaburra showing the two sets of monochromator/analyser channel cut crystals.](image)
The deflected beams enter two sets of fivefold reflection channel cut crystals that can be brought into the Bragg condition alternatively (figure 2). The first set of two perfect Si (111) oriented crystals reflects the 4.74 Å neutrons at a Bragg angle of 49.1° while the second set of two Si (311) oriented crystals reflects the 2.37 Å neutrons at a Bragg angle of 46.4°. Figure 3 gives an impression of the size of the channel cut crystals and describes the way they were cut out of a 100 mm diameter float zone ingot. The <110> growth axis is typically 6° off the cylinder axis. It is seen that the maximum size is limited by the diameter of the ingot and the angular offset.

Figure 3. Cutting scheme of the channel cut crystals. Left: section view of the ingot. Right: top view.

3. Theoretical background
In publications referring to USANS and USAXS techniques, see e.g. [1], the multiple reflection curves are usually given according to two cases, the Darwin and the Ewald case. The first holds if absorption is so big that reflections from the back face of the crystals can be neglected which is typical for X-rays, or if such reflections can be avoided by special crystal shapes for neutrons that penetrate typically several cm into materials such as Si.

For the Darwin case the diffraction curve is given by

\[ R_D(y) = \frac{P_D}{P_e} = \begin{cases} 1 & |y| \leq 1 \\ \frac{y}{\sqrt{y^2 - 1}} & |y| > 1 \end{cases} \]

(1)

whereas the Ewald solution yields

\[ R(y) = \frac{P_E}{P_e} = \begin{cases} 1 & |y| \leq 1 \\ 1 - \frac{1}{y^2} & |y| > 1 \end{cases} \]

(2)

where \( y \) is a dimensionless parameter that is half the width of the Darwin plateau. On the angular scale the full width, \( \Delta \theta_b \), is obtained as

\[ \Delta \theta_b = 2[\lambda^2/\sin 2\theta_b][|F(h,k,l)|e^{-W/\pi V_o}] \]

(3)

where \( \lambda \) is the wavelength, \( \theta_b \) the Bragg angle, \( F(h,k,l) \) the structure factor containing the coherent scattering length, \( e^{-W/\pi V_o} \) the Debye-Waller factor where \( W = B/(2d_{hkl})^2 \), \( d_{hkl} \) the lattice plane spacing, \( B \) a parameter depending on the Debye temperature and \( V_o \) the unit cell volume. Specifically for the Si (311) reflection relevant for this study, a Bragg angle of \( \theta_b = 46.4^\circ \) and \( \lambda = 2.37 \) Å we get \( \Delta \theta_b = 5.04 \) µrad or about 1 arcsec. In the case of a single reflection we obtain for the full width at half maximum 5.82 and 5.35 µrad for the Ewald and the Darwin case, respectively, i.e. a difference of about 9% between the two solutions. This difference should be easily observable experimentally.
Figures 4 and 5 show the universal theoretical diffraction profiles and the double-crystal rocking curves, respectively, for perfect crystals and negligibly small absorption. The latter condition holds for neutrons attenuation in perfect Si, because the extinction depth of less than typically 10 µm is very small compared to the absorption depth. In addition to the Darwin and Ewald cases a set of third curves is plotted labelled “Bonse” that corresponds to equations given in [7,8] and is identical to the Ewald solution for single reflections. It is seen that the difference between the Darwin and the Ewald curves increases with the number of reflections and with the distance from the peak centre.

4. Crystal designs

In this section we first recall two channel cut crystal designs that permitted to achieve Darwin type rocking curves for neutrons. Then we describe two crystal designs that should allow us to reach the same goal.

Figure 6. Comparison of some published work. The red (full), blue (broken) and green (dotted) curves are the same as in figure 5. The curve assignments are:

1 - ref. [9], experiment, $n = 3$, $m = 3$, Si 111.
2 - ref. [9], theory, $n = 3$, $m = 4$, Ewald.
3 - ref. [9], theory, $n = 5$, $m = 5$, Ewald.
4 - ref. [4], theory and experiment, $n = 3$, $m = 3$, Si 111, Darwin.
5 - ref. [10], theory, $n = 3$, $m = 3$, Ewald.

The numbers $n$ and $m$ designate the number of reflections in the first and the second crystal, respectively.
An overview of experimental results and a comparison with theory is compiled in figure 6. All the calculated Ewald and Darwin curves for $n = m = 3$ and 5 agree perfectly well with each other, as to be expected. Regarding experimental data, excellent agreement with theory has been obtained for $|\gamma| < 4$, even for the Darwin case [4], but significant deviations occur for $|\gamma| > 4$.

4.1. Existing designs

The two crystal designs achieving the Darwin type rocking curves are shown in figure 7. In the first case (figure 7a) the crystal reflectors were made so thick that the part of the neutron beam hitting the back side of the crystal could not reach the front face after reflection. In this way the term that contributes to reflection from the backside, which gives rise to the broader Ewald profile, was suppressed. Indeed, perfect agreement with the Darwin theory was found.

![Figure 7a](image1.png) Crystal design according to ref. [4].

![Figure 7b](image2.png) Crystal design according to ref. [5].

In the second case (figure 7b) the crystals were given a triangular shape so that the neutrons did again not “see” any back side parallel to the front side [5]. Thus the broadening term, see figure 6 in ref. [5], was suppressed as shown experimentally, see figure 10 in ref. [5]. In addition, both geometries permitted to reduce thermal diffuse scattering that otherwise would contribute to the general background.

4.2. Proposed designs

![Figure 8](image3.png) Slotted crystal back to avoid reflections from the rear face. The slots are to be filled with a neutron absorbing material such as cadmium. The neutron beam cannot “see” the back face at all (see broken line). Condition: $c/d > \tan \theta$ where $\theta$ is the Bragg angle.
The neutron beam size and the crystal size restrictions for *Kookaburra* shown in figure 3 made it impossible to apply the designs shown in figure 7. Therefore another design was imagined following the principle that the neutrons should not see the back face or, if they see it, they should not be able to interfere with the reflection from the front face. The principles of the two proposals are shown in figures 8 and 9.

![Figure 9](image1.png)

**Figure 9.** Same design as in figure 9 but with fewer slots. Part of the neutron beam can “see” the back face but cannot escape to the front because of the absorbing material (not shown in the figure) by the cadmium, see the broken line. Condition: \(2c/d > \tan \theta\).

For both these designs it is very important that at least 100 µm of Si are removed by chemical etching in order to recover the unperturbed, perfect crystal after cutting and fine grinding. This requirement conditioned the width \(w\) of the slots that should be big enough to allow for easy circulation of the etching liquid. A slight rounding of the bottom due to the shape of the cutting tool and the etching occurred that could lead to a small effect on the Darwin profile.

The design shown in figure 9 is a simplified version of the design in figure 8. Here part of the beam hits the back face but cannot escape to the front because it is absorbed. Typical dimensions of the final channel cut reflectors (Si 311, \(\theta = 46.4^\circ\)) are reflector length \(a = 82\) mm, width \(b = 12\) mm and height \(h = 59\) mm, slot depth \(c = 5\) mm and distance \(d = 9\) mm. The width \(b\) is a compromise between mechanical stability including machining risks and the smallest possible crystal volume giving rise to thermal diffuse scattering.

![Figure 10](image2.png)

**Figure 10.** Sample C (9 slots) and the cadmium absorber inserted in the slots and surrounding the back and the sides of the crystal.

The crystals to be prepared for test experiments on the instrument S18 of the ILL [11] should have the same values for \(b\), \(c\), \(d\) and \(w\) as the final reflector. However, since the beam width at S18 is < 30 mm and its height is < 50 mm, a crystal length of 48 mm and a height of 70 mm were fully sufficient. The three 311 crystals were \(b = 12\) mm thick. Crystal A served as a reference and had no slots. Crystal B had five slots and crystal C 9 slots with a slot distance of 9 mm and 4.5 mm, respectively. The other
dimensions were: slot depth $c = 5$ mm and width $w = 2$ mm. The crystals were manufactured by the company Andrea Holm, Tann, Germany. The reflecting surfaces were fine ground, deep etched and polished using a strain-free chemical-mechanical process. The other surfaces were deep etched. Photographs of the sample with 9 slots and the cadmium absorber are shown in figure 10. As an alternative to Cd as absorber, in a second test run $\text{B}_4\text{C}$ powder (24 $\mu$m mesh) was filled into the slots and kept in place by adhesive tape.

5. Experiment setup and theoretical prediction
The experimental setup on S18 and a rocking curve obtained with crystal A are shown in figure 11. The Bragg angle $\theta_b$ was 45° and the wavelength $\lambda = 2.3158$ Å. Because the perfect monochromator crystal was 110 oriented, the 311 reflection was asymmetric from the 111 oriented side-face. To avoid the part of the beam exiting the 110 front face, a slit was positioned intersecting the unwanted neutrons. The reflected beam was 10 mm wide and 25 mm high. The rocking curve was nicely symmetric. It was flat-topped because the reflection curve at the monochromator exit was 1.9 times wider than the symmetric reflection from the sample.

![Figure 11. Experimental setup on the instrument S18.](image)

The following numerical data have been calculated from dynamical theory, see equation 3.

**Monochromator**
- Asymmetry angle $\alpha = \angle$ between the 311 and the 111 (surface) planes = 29.5°.
- Asymmetry factor: $b^{1/2} = \left[\sin(\theta_b + \alpha)/\sin(\theta_b - \alpha)\right]^{1/2} = 1.900$ for $\theta_b = 45^\circ$.
- Full width of the Darwin plateau, asymmetric geometry: $2y_s = 2y_s \cdot b^{1/2} = \Delta\theta_{D,s} \cdot b^{1/2} = 0.523$ mdeg.
- Full width at half maximum, $\omega_b$, asymmetric case:
  - Ewald case: $\omega_{Ea} = 2\Delta\theta_{D,s} \cdot b^{1/2}/\sqrt{3} = 0.604$ mdeg.
  - Darwin case: $\omega_{Da} = 3\Delta\theta_{D,s} \cdot b^{1/2}/2\sqrt{2} = 0.555$ mdeg.

**Sample**
- Full width at half maximum, $\omega_s$, symmetric case:
  - Ewald case: $\omega_{Es} = 2\Delta\theta_{D,s}/\sqrt{3} = 0.318$ mdeg.
  - Darwin case: $\omega_{Ds} = 3\Delta\theta_{D,s}/2\sqrt{2} = 0.292$ mdeg.

**Convolution of monochromator and sample curves**
a) Convolution factors, 2 x symmetric and 2 x asymmetric geometry, respectively:
  - Ewald case: $f_{E} = \pi/(2\pi - 4) = 1.376$ => total width $\Omega_{E,s} = 0.437$ mdeg; $\Omega_{E,a} = 0.830$ mdeg.
  - Darwin case: $f_{D} = 5/4 = 1.250$ => total width $\Omega_{D,s} = 0.365$ mdeg; $\Omega_{D,a} = 0.693$ mdeg.
b) Convolution, asymmetric (monochromator) plus symmetric (sample) geometry:
The convolution of two perfectly rectangular distributions of widths \( w_1 \) and \( w_2 \) has a trapezoidal shape of FWHM equal to the bigger width. Thus, as a first approximation we get for the convolution of the two diffraction curves a total width of \( \Delta \theta_{b} \cdot b^{1/2} = 0.523 \text{ mdeg} \), multiplied by a smearing factor due to the fact that the Darwin curves are not perfectly rectangular and then by the convolution factor. For simplicity we assume that the width of the convolution of the two curves is the mean of the asymmetric and symmetric widths.

The final results are then for single reflection curves:
- Ewald case: \( \Omega_{Ea+s} = 0.64 \text{ mdeg} \).
- Darwin case: \( \Omega_{Da+s} = 0.53 \text{ mdeg} \).
- Difference of the FWHM between the two cases: 0.1 mdeg or 17%.

The combination of a first, asymmetric monochromator crystal, Ewald case, with a second, symmetric sample crystal, Darwin case, would give a width somewhere in-between the Ewald and the Darwin case (mixed Ewald-Darwin case), say, in the middle at 0.59 mdeg.

6. Experimental results, discussion and conclusion
Typical examples of rocking curves over a wide angular range and in the central part are given in figure 11. They have been obtained from the reference crystal without slots.

![Figure 12a. Rocking curve over a wide angular range for crystal A.](image)

![Figure 12b. Central part of the rocking curve shown in figure 12a.](image)

![Figure 13. The FWHM of the rocking curves for the following crystal cases:](image)

1. A – no grooves
2. B – 5 grooves, no absorber, first run
3. B – 5 grooves, no absorber, second run
4. C – 9 grooves, no absorber
5. B – 5 slots filled with Cd
6. C – 9 slots filled with Cd
7. B – 5 slots filled with B_{4}C powder
8. C – 9 slots filled with B_{4}C powder
9. Backside of a big channel cut crystal
The red vertical lines are the error bars.

The results of the rocking curve full width at half height are summarised in figure 13.
Figure 14. The decrease of the rocking curves in the wings. Left: low-angle side; right: high angle side. The angular scan range of ± 100 µrad corresponds to a range of ± 42 for y.

We found very good agreement of the theoretical Ewald FWHM with the experimental result of (0.66 ± 0.01) mdeg observed for crystal A (no slots) showing that the calculation of the convoluted curve and the crystal preparation and mounting have been correct. The smallest value of (0.65 ± 0.01) mdeg for the width of the slotted crystals was obtained for crystal B with B₄C powder in the slots. Within the experimental error this value was identical with the result for crystal A and for the backside of a channel cut crystal. It was above the theoretical result of 0.58 mdeg for the mixed Ewald-Darwin case. For the very far wings crystal C with B₄C in the slots gave the smallest intensities, see figure 14. The 0.01 reflectivity level is crossed at a rocking angle of ± 33 µrad or y = ± 14. This is slightly above the theoretical values for the Ewald case as shown in figure 6 for two single reflections.

The crystals with empty slots exhibited an increase of the rocking curve width outside the error bars above that of the Ewald case, see figure 13. To make sure that there was no experimental error we remeasured the width for crystal B in a second run after dismounting and remounting the crystal and realignment of the vertical tilt angle. The increase was bigger for crystal B (5 slots) than for crystal C (9 slots), which is counterintuitive when supposing that the presence of slots introduces a perturbation of the dynamical wavefield inside the crystals. It could not be ascribed to residual strains. When filling the slots with an absorber, the width of the diffraction profiles decreased, but without reaching that of the Darwin curve. Filling the slots with B₄C gave slightly better results than using Cd, which might be due to a better contact of the powder with the groove walls. It is also interesting to note that according to the experiment the reflection curve of the first (monochromator) crystal used on S18 seemed to be of the Ewald type although the neutrons hitting the rear crystal face were eliminated by the slit, see figure 11, and thus the Darwin case should apply.

In conclusion, the results for the widths at half maximum and in the wings did not indicate any shift from the Ewald type diffraction curves towards the Darwin type ones when using the grooved crystals with absorbers. Understanding the experimental results of the present study and determining a successful crystal design for achieving Darwin type rocking curves call for the development of a theory that permits to describe neutron diffraction from crystals with a back face that is different from flat. A theory based on a finite element approach integrated into dynamical theory is presently being developed [12]. First promising results have already been obtained and work is in progress.

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