Recent studies of highly oriented pyrolytic graphite and hybrid graphite-silicon monochromator systems

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Abstract The excellent performance of highly oriented pyrolytic graphite (HOPG) as monochromator, analyzer and filter material for neutron instrumentation was discovered more than 50 years ago. Even though HOPG has been in use for a long time, there is still room for improvements regarding its optimized use in neutron beam conditioning. The features of a novel concept called POSI based on careful x-ray characterization of the HOPG crystals and on proven mounting and focusing technologies show that the efficiency of HOPG monochromators can be increased while decreasing complexity and cost. Moreover, by combining HOPG and bent perfect silicon crystals the functionality of separate single monochromators and analyzers can be expanded to a wider range of applications provided by dual systems or bichromators.

1 Introduction

The superiority of highly oriented pyrolytic graphite (HOPG) as a material for neutron beam conditioning is well established. When comparing both the nuclear scattering properties and the structural data with those of potentially competing materials, only diamond and beryllium show similar performances as neutron monochromators and analyzers. The figures of merit normalized to that of HOPG are 1.2 for diamond and 0.96 for beryllium, followed by 0.55 for lead, 0.51 for silicon, 0.40 for niobium, 0.35 for germanium and 0.26 for copper, respectively [1]. This theoretical approach assumes that these materials would be available as ideal mosaic crystals featuring a mosaic spread of typically 0.2° to 1°.

Based on these predictions considerable efforts to produce beryllium and diamond mosaic crystals with uniform defect structures were undertaken in the past. They did not succeed because of the unfavourable defect and mechanical properties of these materials. By the way, the Greek root of the word diamond signifies the “*untameable*”. Thus a reproducible monochromator production on a large scale could not be envisaged. The development of niobium crystals strained by diffusion of deuterium had to be abandoned, too. Nowadays, plastically deformed copper, germanium and silicon mosaic crystals are applied in addition to HOPG. Copper is preferred for the short wavelength range because of its small unit cell while germanium and silicon single crystals permit to suppress second order reflections. Their mosaic distribution is relatively uniform. It can be made anisotropic which is an advantage, in particular for increasing the focusing efficiency in vertical (sagittal) direction where the smaller mosaic spread diminishes the beam widening.

As an alternative to mosaic crystals, nearly perfect, bent silicon crystals were introduced successfully as monochromators, see *e.g.* refs. [2-4]. Elastic bending permits to focus the reflected neutron beam and creates lattice deformations that increase the integrated reflectivity per unit volume. The diffraction process can be well described by a modified dynamical theory. To obtain sufficient intensity a thickness of about 10mm is required. To prevent breakage when bending silicon blades, these monochromators are made of stacks containing typically ten blades of 1mm thickness. Their neutron rocking curve width is smaller than that produced by HOPG which results in higher spectral resolution at the expense of integrated intensity. On the other hand, the five times bigger thickness of the silicon stacks leads to a widening of the monochromatic beam that increases the focal spot size. However, the global performance of bent silicon crystals is still quite high. An advantage of silicon is the possibility to use asymmetric reflections in both reflection and transmission geometry. The latter is applicable only if there is no material in the beam trajectory behind the stack.

The specific properties of mosaic HOPG and bent silicon crystals make them complementary. Therefore, many instruments employ several monochromators. Their number and the materials depend on the spectral resolution and the neutron wavelength range. Usually three- or four-face monochromators are mounted on turrets located inside the monochromator housing. As an example, the three axis spectrometer IN8 at the Institute Laue-Langevin uses a triple device consisting of double focusing HOPG and copper mosaic crystal systems plus a stack of bent silicon crystals with fixed horizontal and variable vertical curvature [5].

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In a scenario called serial beam multiplexing, two (or more) instruments are placed one behind the other on the same neutron source, for example on a guide. Here the downstream instrument is fed by the neutron beam exiting the upstream monochromator. Therefore the transmission of the upstream device should be as high as possible. For example, this scheme was applied at the USANS instrument Kookaburra at ANSTO [6]. The HOPG crystals composing the double focusing premonochromator were soldered on a perfect silicon support plate of toroidal shape.

A very elegant design of a different type of double focusing monochromator was reported for a triple axis spectrometer at NIST [7, 8]. Variable vertical curvature was achieved by buckling specially shaped, vertically aligned aluminium support plates carrying the HOPG crystals. Horizontal focusing is obtained by rotating the support plates around a vertical axis.

A still different system was fabricated recently by the company Positechnics, France, for the texture diffractometer HETU at the China Mianyang research reactor, CMRR [9-11]. A fixed horizontal curvature was generated by soldering Momentive ZYA-N grade HOPG crystals on faceted perfect silicon support plates made by the company Siliciumbearbeitung Andrea Holm GmbH, Germany. These plates were mounted on a mechanical device allowing for variable focusing in vertical direction by rotation about horizontal axes.

In this paper we outline recent attempts to further perfect the neutron monochromator technology. We propose hybrid schemes regarding the application of HOPG combined with bent perfect silicon crystals. These compact double or dual HOPG-silicon systems also minimize the intensity loss of the non-diffracted, throughgoing neutron beam. We begin by briefly recalling the scattering properties of HOPG and by describing the x-ray characterization of the HOPG crystals delivered by Momentive Technologies that are beneficial for optimizing composite HOPG systems.

2 Neutron scattering properties of PG

The scattering properties of imperfect crystals depend on the radiation used. They are calculated theoretically by the kinematical approximation applied to the so-called mosaic model assuming that the diffracting crystal can be regarded as a homogeneous assembly of independently scattering volumes called mosaic blocks that represents the defect structure of real crystals.

These crystal domains are considered to be perfect inside and small enough so that dynamical diffraction effects can be neglected. But to avoid beam widening and particle size broadening of the diffraction pattern they should not be too small as well. The orientation of these mosaic blocks is supposed to follow a Gaussian distribution function. For several reasons all these conditions characterizing the so-called "ideal mosaic crystal" are never fulfilled by a real, non-perfect crystal containing defects such as dislocations that are most frequently arranged in small angle grain boundaries. The main deviations from the model are caused by non-uniformities of the spatial and angular strain distributions. The experimental rocking curves shown in fig. 1 can be matched by a double mosaicity, a deviation from a purely Gaussian angular mosaic block distribution and by the effect of primary extinction due to a mosaic block size exceeding what is called the primary extinction thickness. This effect decreases the peak reflectivity.

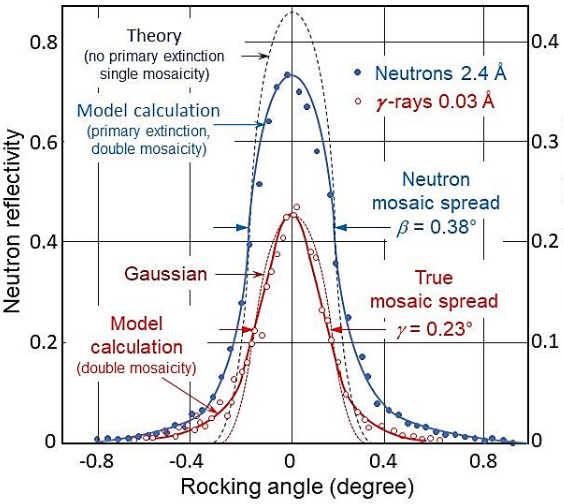

Fig. 1. Neutron and γ-ray rocking curves of a HOPG-ZYA grade sample [11].

When attempting to predict the monochromatic flux obtained by mosaic crystals, for example by using computer simulations, it is important to consider the fact that there is a difference between what we call the *true mosaic spread, γ,* that can be measured almost extinction-free by high-energy γ-rays, the *x-ray mosaic spread, ξ,* that is the FWHM of the x-ray rocking curve, and the wavelength dependent *neutron mosaic spread, β,* that corresponds to the FWHM of the neutron rocking curve. The empirical correlation of these three quantities is displayed in fig. 2.

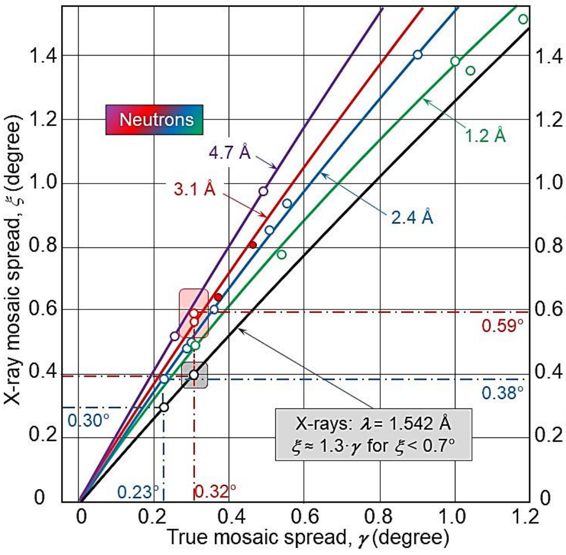

Fig. 2. Correlation between the true mosaic spread measured with short wavelength (0.03Å) γ-rays and the FWHM of x-ray and neutron rocking curves, HOPG 002-reflection, depending on the grade of the samples [11].

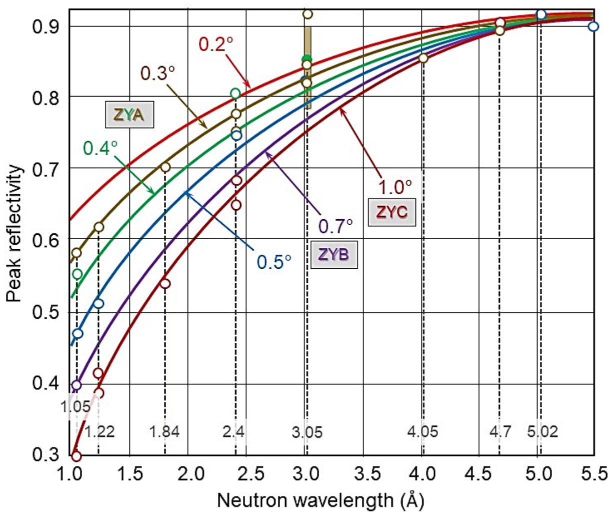

Fig. 3. Experimental peak reflectivities of Momentive ZYA, ZYB and ZYC grade HOPG as a function of wavelength and true mosaic spread for a crystal thickness of about 2 mm [11].

For example, a crystal characterized by x-rays of 1.542 Å wavelength producing a 0.40° wide rocking curve exhibits a true mosaic spread of 0.32° when recorded by diffraction of γ-rays of 0.03Å wavelength in transmission geometry. The corresponding mosaic spread for neutrons of wavelength 3.1Å is 0.59°, almost twice the true mosaic spread. The curves shown in figs. 2 and 3 are averages of results obtained for many samples. The range of measured values is indicated by the shaded areas. At certain wavelengths competing HOPG reflections are excited that influence the width and the peak reflectivity. Thus the smoothened curves represent approximations. However, these data can be used for resolution and flux estimations based on computer simulations. For more details see ref. [11] and the literature cited therein.

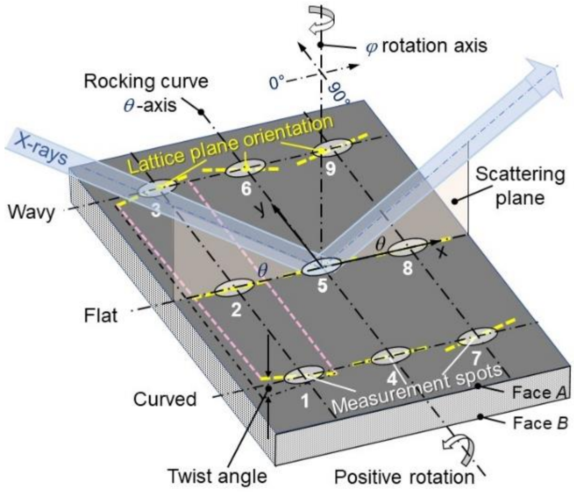

Fig. 4. Diagram of x-ray tests performed by Momentive Technologies to determine the mosaic spread and the lattice plane orientation of HOPG typically 20x20mm² in size.

Detailed x-ray diffraction tests of HOPG crystals proved to be very useful and sufficient for optimizing position and orientation of the pieces in the matrix of composite monochromator systems. By scanning a typically 1mm² wide x-ray beam across the surface of the sample with high spatial resolution, the topology of the lattice plane orientation is recorded in much more detail than with neutron beams. As shown below in fig. 4, three types of lattice plane orientation changes are observed: a wavy behaviour, a flat shape and a uniform curvature. The crystals are studied in two azimuthal positions and on both faces. The data obtained allow us to identify the concave face to be turned towards the incident neutron beam and to select the best samples to be placed in the center of the composite system.

3 Focusing devices

A drawback of HOPG is its strong mechanical rigidity and its fragility that prevent the creation of variable crystal curvature by elastic bending. Therefore, the majority of today's single and double focusing devices consist of typically 20x20mm² wide, more or less flat pieces. They are mounted on mechanical systems where each piece can be aligned individually by a mechanical lever-cam system to achieve fixed or variable meridional and/or sagittal focusing, see the photograph in fig. 4. To protect the mechanical parts situated behind the crystals against neutron and γ-ray irradiation, the crystal supports are covered by a neutron absorbing material, for example B_4C. Then the non-diffracted quasi-white neutron beam is blocked and cannot feed other instruments situated downstream that otherwise could use neutrons exiting from the same source.

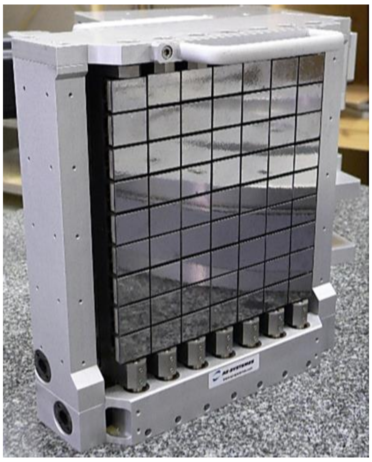

Fig. 5. Conventional double-focusing monochromator composed of HOPG mosaic crystals bonded on individually orientable supports. (Courtesy: Positechnics).

In an attempt to achieve dynamical focusing by a variable curvature of the HOPG crystals, the bendability of Momentive grade ZYA crystals was studied as a function of their thickness and curvature. To achieve a minimum radius of 1.5m without breakage the thickness had to be inferior to 0.1mm, but even then a non-zero risk of damage after several bending and flattening cycles remained [12]. The results also showed that the elasticity limit was sample dependent. Therefore, the idea of bending thin HOPG blades for dynamical focusing was not followed up.

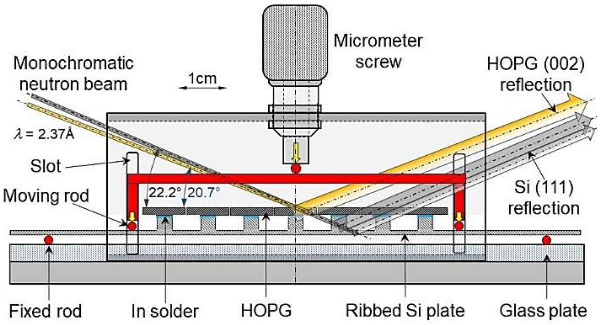

Fig. 6. Schematic view of the four-point bending device for studying the POSI system and the neutron diffraction geometry used for the tests [12].

Fig. 7. A long HOPG crystal indium bonded on a ribbed silicon blade and then sliced into 9mm wide segments.

An alternative design was examined where flat HOPG crystals are soldered onto a bendable, ribbed silicon plates, supplied by Siliciumbearbeitung Andrea Holm GmbH, Germany. This concept is called POSI, an acronym for **p**yrolytic graphite **o**n **si**licon. The use of ribs decreases the amount of stress on the indium bonds created by bending the plates and thus avoids the risk of detachment. Mechanical and both x-ray and neutron diffraction tests using the device shown in fig. 6 confirmed that this new type of monochromator with precise, tunable curvature can be safely used in neutron instrumentation [12]. A photograph of the assembly is presented in fig. 7.

Similar to the design described in refs. [7] and [8] the POSI device is mechanically less complex than the conventional scheme. In comparison with the buckling technique of aluminum blades the use of silicon perfect crystals as support material reduces the background produced by Bragg scattering. The four-point bending design does not require the complex shape of the support needed for buckling.

The POSI design has the same advantage of transmitting the non-diffracted neutron beam with a minimum loss to the instruments located further downstream on the same beam tube or neutron guide that can be arranged according to an optimal sequence [13]. The length reduction of the individual HOPG pieces could improve the uniformity of the global curvature. This would improve the monochromator efficiency for thermal neutrons and under high resolution conditions where the beam divergence and the width of the neutron rocking curves are small.

But this is not the end of the story. A material called glassy carbon commercialized under the name Sigradur, well characterized with neutrons [14], will replace the perfect silicon support plates. Then the acronym POSI stands for 'pyrolytic graphite on Sigradur' too. When compared to silicon, in addition to the advantages of smaller attenuation and less thermal diffuse scattering, this amorphous material does not produce parasitic Bragg scattering. Sigradur type G plates can be obtained from the company Hochtemperatur-Werkstoffe GmbH, Thierhaupten, Germany.

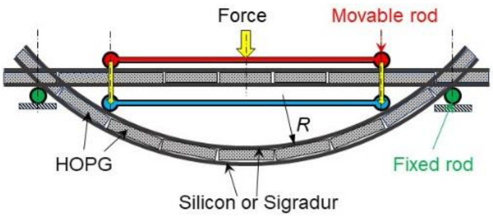

Fig. 8. Four-point bending principle acting on a sandwich of HOPG crystals and silicon or glassy carbon plates.

The system shown in fig. 8 is presently studied. It does not use any bonding material. To ascertain a uniform curvature very precise dimensioning of the HOPG pieces is required. In view of the varying shapes and dimensions of these pieces this condition is likely to represent a challenging technical difficulty.

4 Dual and double monochromators

The POSI technique permits to integrate individual HOPG and silicon monochromators into single devices. For example, by adding a ribbed Si crystal carrying the HOPG pieces or a Sigradur-HOPG sandwich on top of a stack of Si blades, using *e.g.* the device shown in fig. 9, a bichromator, is formed.

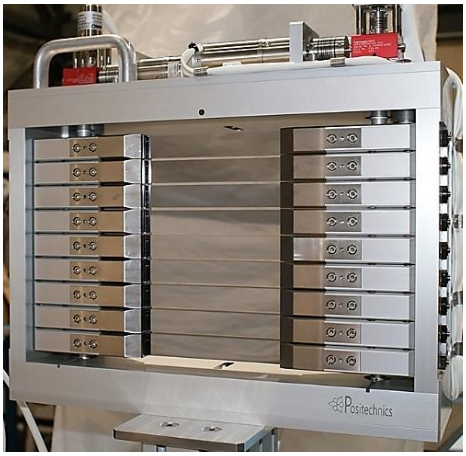

Fig. 9. Conventional double-focusing silicon monochromator with variable curvature composed of bent stacks of typically 10 perfect crystals each. (Courtesy: Positechnics).

Such a system extracts simultaneously two monochromatic neutron beams of different flux and spectral resolution out of a white incident beam; see the example shown in fig. 10. Depending on the degree of asymmetry and on the Bragg reflection of the silicon crystals they focus neutrons of the same or of different wavelength(s) with respect to the neutrons scattered by the HOPG crystal. The beams produced by dual reflections can be received by one or two sample(s), either simultaneously or one after the other. If no obstacles are situated behind the crystals, neutrons diffracted in symmetric or asymmetric transmission geometry of the silicon crystals can be used too.

As an illustration of possible hybrid scenarios we present the application of the POSI design principle to a monochromator actually requested for the ANDES stress diffractometer that is planned to be installed at the LAHN facility presently under construction in Bariloche, Argentina (https://www.lahn.cnea.gov.ar/).

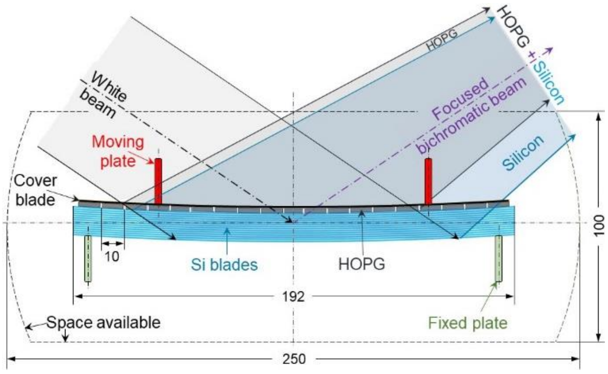

Fig. 10. Top view of one stack of a hybrid HOPG-Silicon monochromator proposed for the instrument ANDES focusing two neutron beams of slightly different wavelengths simultaneously on the same sample position. The dimensions are mm.

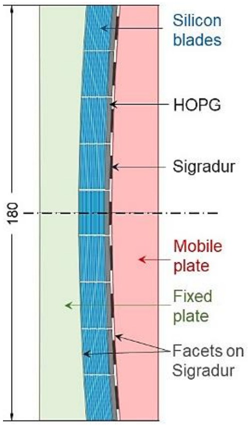

Fig. 11. Side view of the dual monochromator composed of 9 stacks shown in fig. 10.

Figs. 10 and 11 show schematically the proposed hybrid monochromator consisting of stacks of perfect silicon blades carrying 19 HOPG crystals each. The HOPG pieces are covered by Sigradur plates to spread out the local pressure of the force acting on the HOPG crystals and to uniformize the curvature approximated by the crystal polygon. The dimensions were adapted to the relatively small space inside the monochromator vessel of the ANDES device. Instead of the rods shown in figs. 7 and 8, this four-point bending system uses faceted plates made of Sigradur whose shapes are designed for fixed vertical focusing, see fig. 11. The attenuation of the incident and reflected neutron beams traversing these plates is very small.

Two POSI scenarios and a dual system are presented in fig. 12. In line with the specifications, in all three scenarios the constant vertical radius of curvature corresponds to the central wavelength used. The horizontal focusing distance can be kept constant when changing the Bragg angle by adapting the curvature of the HOPG-silicon stacks.

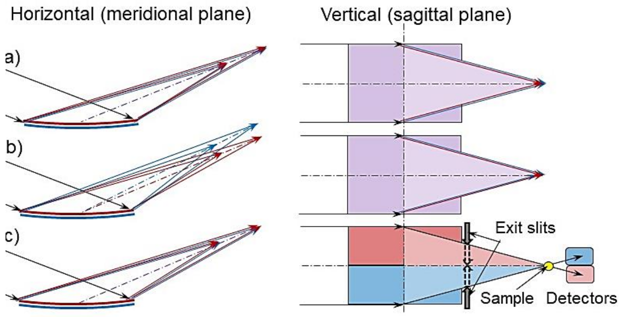

Fig. 12. Three horizontal (left) and vertical (right) geometries of a dual POSI monochromator (a, b) and of a double HOPG-silicon device (c) for two radii of meridional curvature, respectively.

a) Reflected by the HOPG crystals and by the silicon crystals in symmetric geometry a dual beam containing two wavelengths is focused simultaneously on the sample. An example of this option is shown in fig. 10. Here the HOPG (002)- and the silicon (111)-reflections were chosen. Because their *d*-spacings are quite similar, the two corresponding diffraction peaks of the sample are close to each other.

b) When using asymmetric reflection geometries the lattice planes of the silicon monochromator are not parallel to the HOPG lattice planes and the sample will be exposed successively to the two beams by moving it to the respective focal positions. If the sample is wide enough it can intercept both beams.

c) The upper half of the monochromator consists of HOPG crystals, whereas the lower part is composed of silicon stacks. This double monochromator scenario allows us to choose between three possibilities that can be selected by an appropriate positioning of the slits at the monochromator entrance or exit.

i) By shielding the lower half of the double monochromator, the sample receives neutrons only from the HOPG crystals. After reflection by the sample they are recorded by the lower detector.

ii) By shielding the upper half of the double monochromator, the sample receives neutrons only from the Si crystals. After diffraction by the sample they are received by the upper detector.

iii) When the slits are fully open, the sample receives neutrons from both the HOPG and the silicon crystals. The corresponding neutrons scattered by the sample are recorded separately by the upper and lower detector, respectively.

A simultaneous recording of the sample response to the high resolution/low intensity beam and the low resolution/high intensity beam, respectively, is possible for a specific scattering geometry. Such a configuration can be interesting for time-dependent experiments, especially when studying irreversible processes in real-time. An interesting feature of scenario c), case ii), is the availability of a ‘clean’ beam reflected by the Si crystals only. This is not possible for the options a) and b) where the dual wavelength beam focused on the sample may be contaminated by some parasitic Bragg reflections of the HOPG crystals other than the (002) reflection.

5 Summary

The neutron diffraction properties of highly oriented pyrolytic graphite crystals and their application in focusing monochromator and analyzer systems are briefly recalled. The detailed x-ray characterization carried out routinely by Momentive Technologies appears to be sufficient to optimize such composite systems as a function of the shape and the mosaicity of the HOPG crystals. The relation between the intrinsic mosaic spread of this material, the widths of x-ray diffraction curves and the wavelength dependence of neutron rocking curves are emphasized. These data can be useful for computer simulations of instrument performance.

Recent bendability studies of HOPG showed that elastic bending of this material to achieve dynamical focusing of neutron beams is unrealistic. A novel technique called POSI that is different from the presently used mechanical focusing devices has been tested successfully where approximately flat HOPG pieces are bonded on the ribs of flexible silicon plates. This technique has the advantage that the non-diffracted, quasi-white beam is transmitted with only small attenuation to instruments situated downstream on the same neutron guide. Compared to the properties of aluminum and silicon as support materials the use of bendable plates made of glassy carbon would still increase the transmissivity of POSI monochromators and decrease the background intensity. When holding the HOPG crystals between two glassy carbon blades, any glue or solder might become unnecessary. This possibility is presently being studied.

The complementarity of HOPG and bent perfect silicon crystals suggests their use in hybrid systems where both materials are integrated into compact bichromator devices. Neutron scattering experiments can then be conducted, either simultaneously or successively, under high flux-low resolution and low flux-high resolution conditions. The POSI technique is a perfect tool to realize such scenarios. An example is given describing an application to a strain analysis diffractometer that is presently in the design status.

Because of their increased functionality, reduced size and complexity, bichromators are cost-effective and thus attractive from both ecological and economical viewpoints. Similar considerations may apply to crystal analyzer systems. Frontend monochromator multiplexing using different materials might be interesting when correlated with backend analyzer multiplexing techniques presently applied or proposed [15, 16].

The choice of the most suitable dual or double monochromator option for a given experimental study is determined by the best compromise between a multipurpose scenario and a highly specific mode of instrument operation. The hybrid concept as presented in this paper is meant to be a first step towards an alternative kind of monochromator design. We trust that it will find useful applications.

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