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# CHARACTERISTICS OF PYROLYTIC GRAPHITE AS AN ANALYZER AND HIGHER ORDER FILTER IN NEUTRON SCATTERING EXPERIMENTS*

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Pyrolytic graphite (PG) has become nearly indispensable in neutron spectroscopy. Its use as a monochromator and/or analyzer crystal in a triple-axis spectrometer has previously been discussed. Since the reflectivity varies as a function of energy, observed neutron intensities must be corrected for the analyzer reflectivity. Presented here are detailed measurements of the reflectivity of the (002) reflection for incident neutron energies from 4.5 to 40.0 meV. There are relatively large dips at 15.3 and 23.6 meV which result from competing Bragg reflections. We also point out that the width of the rocking curve increases as the energy is decreased. This must be considered when making resolution function corrections. PG in bulk form has been extremely useful as a higher order filter in the 13.0–15.0 meV range. It is shown below that it can also be used effectively in the very low energy range, 4.5–6.0 meV.

## 1. Introduction

The development of the triple-axis spectrometer for inelastic neutron scattering has proved invaluable for measuring excitations in solids, liquids, and gases. This spectrometer requires a monochromator to select a single incident neutron energy and an analyzer to determine the energy of neutrons scattered from a sample. The use of highly oriented pyrolytic graphite (PG) as monochromators and analyzers has enhanced the efficiency of the triple-axis spectrometer. PG has a preferred orientation of the (00*l*) planes with the other (*hkl*) planes aligned randomly within the crystal. Due to this randomness, primary extinction is greatly reduced from that of single crystals with a resultant increase in reflectivity. The peak reflectivity is defined as the reflectivity when the crystal is set at the Bragg scattering angle. Riste and Otnes[1]) have measured peak reflectivities of PG as high as 74% at 50 meV. At this energy, the reflectivities of Ge(111) and Be(002) are 22% and 42%[1]) respectively. Furthermore, Riste[2]) suggested that the neutron flux can be further increased by bending the monochromator to a cylindrical surface. Nunes and Shirane[3]) have shown that the use of a vertically bent PG monochromator can increase the intensity by a factor as high as 3.5 with no change in resolution. The use of bent monochromators has made possible inelastic neutron scattering experiments with samples as small as 0.1 $cm^3$.

Riste and Otnes compared the measured reflectivity of PG to the value calculated from the formulae developed by Bacon[4]) for an ideally imperfect crystal where secondary extinction prevails. It was shown that there is a gradual decrease in reflectivity as the energy increases. We show below that superimposed on this gradual decrease are dips in the reflectivity resulting from competing Bragg reflections. These dips, though appreciable, are not nearly as deep as those observed in a single crystal. In PG, the reflectivity is independent of rotation of the analyzer about the scattering vector. The reflectivity of a single crystal, on the other hand, is extremely sensitive to such a rotation since the competing reflections will move out of or into the scattering plane. For a single crystal, therefore, the experimenter must know the reflectivity for the particular mounting of his analyzer. For PG, however, the reflectivity should not vary among different analyzers except for a possible normalizing factor. The measurements below, therefore, should be useful for any PG analyzer.

Even with this high reflectivity, the use of PG as a monochromator is limited at low energies due to the large amount of higher order energy contamination. Single crystals of materials such as quartz or beryllium have been used to discriminate against higher order energies for the primary energy range 10–50 meV. They,

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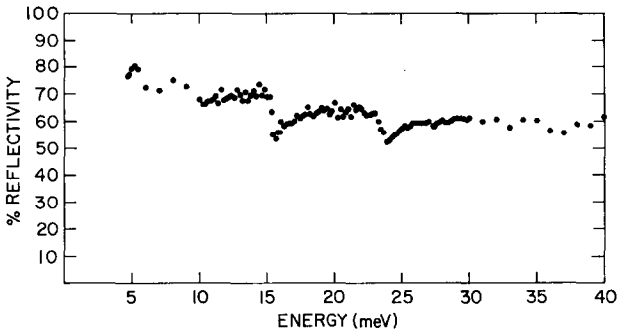


Fig. 1. Energy dependence of pyrolytic graphite (002) reflectivity measured using a chromium sample.

however, have the drawback that sufficient attenuation of higher order neutrons involves a considerable loss of primary neutrons as well.

Brockhouse and Diefendorf[5]) suggested that PG in bulk form is a more suitable filter and Loopstra[6]) first demonstrated its effective use in the low energy (less than 15 meV) range. Shirane and Minkiewicz[7]) have shown that PG crystals with narrow mosaic spread give high transmission of neutrons with primary wavelength $\lambda$ in the energy range 13.0–15.0 meV and a very low transmission of neutrons with wavelength $\lambda/2$. It also has been suggested that PG can serve as a useful filter in the low energy (5.0 meV) region[8]). We present below a detailed study of the filtering properties in this energy range.

## 2. Reflectivity measurements

The reflectivity measurements were made for the (002) reflection of plane pyrolytic graphite crystals with thickness approximately 1/16″. The crystals, supplied by Union Carbide Company[9]) were mounted in the analyzer position of a Brookhaven triple-axis spectrometer. The monochromator was a bent PG (002) crystal.

At the sample position was placed a single crystal of chromium with mosaic spread less than 0.05°. The (1, $\delta$, 0) "satellites" of chromium were used as the primary scatterer[10]). These satellites are the result of a sinusoidal modulation of the magnetic scattering amplitude. Since $\delta$ is the same for every reciprocal lattice point, there will be no higher order contamination. Twenty-minute horizontal collimation was used for the inpile and exit collimators, with no horizontal collimation after the chromium sample. There was no vertical collimation before the sample but a twenty-minute vertical collimator was placed between the sample and the analyzer.

The reflectivity at a given energy was obtained by taking the ratio of the intensity with the PG crystal in the analyzer position to the intensity with the analyzer removed. The true absorption of the platelet of PG and its aluminum holder was approximately 2%. The incident energy was varied by changing the angle of the monochromator. Fig. 1 shows the measured reflectivity over the energy range of 4.5–40.0 meV. The main features are the pronounced dips at 15.3 and 23.6 meV and a gradual decrease in the reflectivity as the energy increases.

These features can be explained by the following considerations. Since the planes perpendicular to the $c$-axis are randomly oriented with respect to each other, the Bragg points of these planes can be considered to be Bragg rings about the (00$l$) axis. The scattering plane, then, will intersect all of these rings as shown in fig. 2. For certain values of the energy, the Ewald sphere will intersect one or more rings. The Bragg condition will thus be satisfied for several reflections simultaneously. For these energies, part of the beam will be scattered at an angle other than that of the primary scattering. This part of the beam will most likely not enter the detector and a spuriously low counting rate will be obtained[11]).

The Ewald sphere will first touch the Bragg rings in the scattering plane. As the energy increases, the Ewald sphere becomes larger and it will pass through the rings. Since the sphere must pass through the points (000) and (002) and since the rings are concentric about the (00$l$) axis, a ring can never be wholly contained within the sphere. Hence, once the conditions are met

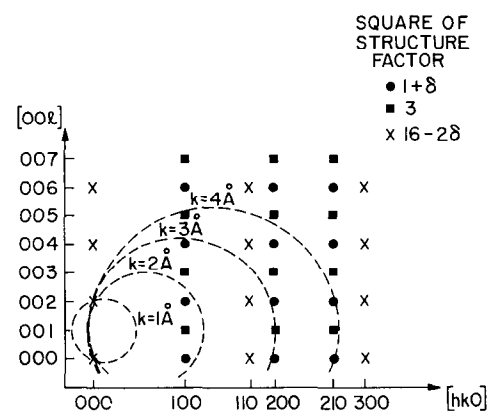


Fig. 2. Scattering plane for the (00$l$) reflection of pyrolytic graphite. It should be noted that the points shown are the intersections of the plane with Bragg rings about the (00$l$) axis. Dashed circles are the intersections of the Ewald sphere for (002) at various values of the wave vector, $k$. $\delta = 8\sin^2(\pi l x)$, where $x \leqslant 0.05$ [12]).

TABLE 1

Calculated positions for parasitic reflections from pyrolytic graphite (002).

| Energy (meV) | $k$ (Å$^{-1}$) | Reflection ($hkl$) | Relative depth |
|---|---|---|---|
| 5.5 | 1.62 | 101 | 3 |
| 6.3 | 1.75 | 102 | 2 |
| 9.5 | 2.14 | 103 | 4 |
| 15.3 | 2.72 | 112 | 15 |
| 16.6 | 2.83 | 104 | 2 |
| 18.9 | 3.02] | 201 | 1 |
| 19.9 | 3.10 | 202 | 1 |
| 22.7 | 3.31 | 203 | 2 |
| 23.6 | 3.32 | 114 | 10 |
| 27.9 | 3.67 | 204 | 1 |
| 30.3 | 3.83 | 105 | 2 |
| 32.5 | 3.96 | 211 | 2 |
| 33.4 | 4.01 | 212 | 1 |
| 36.1 | 4.17 | 205 | } 5 |
| 36.2 | 4.18 | 213 | |

for a particular parasitic reflection, it will continue to "eat" away part of the beam. The dips, therefore, are expected to be sharp on the low energy side (where the Bragg ring is tangent to the Ewald sphere) and to tail off on the high energy side as the sphere moves through the ring. As the energy increases, the superposition of many of these "tails", coupled with the decrease of the crystallographic quantity, $Q$, leads to the general decrease in the reflectivity.

The reflections and energies for which these dips can first be expected to appear are given in table 1. The relative magnitudes of these dips should be approximately the product of the multiplicities, structure factor, and intensity of the Bragg peaks. From table 1, we see that the largest dips should be at 15.3 and 23.6 meV from reflections (112) and (114) respectively. This is verified by the data in fig. 1. Our measured values of the reflectivity are about 10% lower than the values calculated from the equations given by Bacon[4]). A possible explanation, in addition to the superposition of the "tails" mentioned above, is that the peak reflectivity is defined for a non-divergent incident neutron beam. Since we used finite collimation and crystals with finite mosaic spread, we were actually measuring a reflectivity averaged over the effective divergence angle of the spectrometer. This would result in a general lowering of the observed reflectivity. The magnitude of the effective reflectivity, therefore, is dependent upon the experimental arrangement. However, the relative change of the reflectivity with energy, and the location and relative depths of the dips are essentially independent of the experimental arrangement. These are the useful quantities in correcting data.

We have also measured the rocking curve of the PG analyzer crystals at several energies using a perfect germanium sample and twenty-minute horizontal collimation throughout. The observed linewidth increased from 0.56° at 25 meV to 0.63° at 5 meV. This effect has been predicted by Bacon and Lowde[4]) for an ideally imperfect crystal where secondary extinction prevails. Their expression for the reflectivity of an imperfect crystal with no absorption [eq. (3.11) of ref. 4] shows that as the energy decreases, the crystallographic quantity $Q$ becomes large and the shape of the rocking curve changes from a Gaussian (if the mosaic distribution is Gaussian) to a flat-topped curve with a larger full width at half maximum. This effect has also been observed in Pb(111) and Cu(220)[13]). Thus, in an experiment where very accurate resolution corrections are necessary, it is important that the rocking curves of the monochromator and analyzer

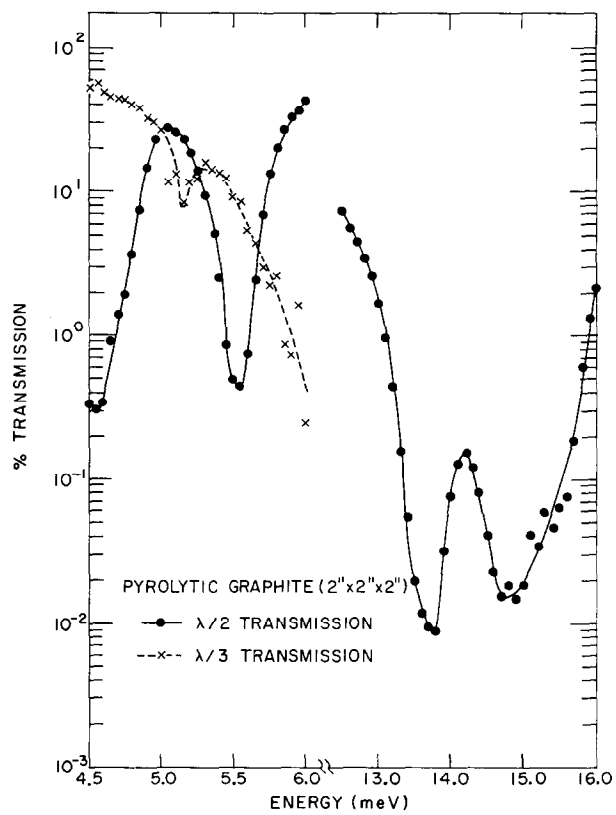


Fig. 3. Higher order transmission of a pyrolytic graphite filter at low energies. The transmission for neutrons of wavelength $\lambda$ in the 2″ × 2″ × 2″ block is ≈78%. The data for 12.5–16.0 meV is similar to that of Shirane and Minkiewicz[7]).

be measured at the energies being used and these values of the full width at half maximum be used in the resolution function calculation.

## 3. Filter properties

It has been shown that PG crystals in bulk form are useful as higher order energy filters[6,7,8]). Because the hexagonal $c$-axes are aligned, neutrons of a certain energy travelling parallel to $c$ will pass through unattenuated. However, the higher energy neutrons will be strongly attenuated by Bragg scattering from other planes in the crystal. This attenuation can be visualized with the aid of fig. 2. When the filter is properly tuned, the diameter of the Ewald sphere lies along the [00$l$] direction. For some given neutron wave vector $2\boldsymbol{k}$ ($k = 2\pi/\lambda$), the Bragg rings will lie along the circumference of the Ewald sphere. This results in large attenuation of neutrons of wave vector $2\boldsymbol{k}$, but generally little attenuation of neutrons of wave vector $\boldsymbol{k}$. Shirane and Minkiewicz[7]) demonstrated the tunability of narrow mosaic PG filters in the primary energy range 13–15 meV. We present here data showing that PG can also serve as an effective higher order filter in the low primary energy range 4.5–6.0 meV.

These room temperature measurements were made with the chromium satellite, thus providing well-defined energies. The PG filter had a thickness of 2″ with a 2″ × 2″ cross section. Fig. 3 shows the results for higher order transmission in the energy ranges 4.5–6.0 meV and 12.5–16.0 meV. The results for the higher range are similar to those of ref. 7. The transmission for neutrons with wavelenth $\lambda$ is 80% in the 4.5–6.0 meV region and 78% at 13.5 meV. We note two minima in the 4.5–6.0 meV region where the $\lambda/2$ transmission is less than 2.5%. These two minima correspond to Bragg reflections from the (103) and (104) planes at 4.6 meV and (102) and (105) planes at 5.5 meV. The $\lambda/3$ transmission also shows two minima, with the deepest still decreasing at the limit of the measurements, 6.0 meV. Where these two curves intersect (5.65 meV) the transmission for higher order neutrons is only 4%.

It is recognized that large pieces of cooled polycrystalline beryllium serve as better filters in this low energy region, but it is not always convenient to cool and position large beryllium samples. The above demonstrate that at 5.65 meV PG can serve as a convenient and reasonable filter where complete attenuation is not necessary.

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