

The Reflectivity of a Pyrolytic Graphite Monochromator

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(Received 21 September 1981; accepted 28 June 1982)

Abstract

It is shown that a pyrolytic graphite monochromator crystal scatters X-rays as a mosaic crystal in accordance with the Darwin formulism, both for reflecting power and integrated intensity, over a range in wavelength from 0.5 to 1.54 Å. The scattering cannot be considered kinematic and, from estimates of the reflectivities parallel and perpendicular to the diffraction plane, polarization ratios are calculated which are in accord with published values. A simple description of the scattering process is given. The variation of polarization ratio with mosaic spread is discussed.

Introduction

Crystals of pyrolytic graphite are now used extensively as monochromators since, being composed of layers of parallel atoms, X-rays are efficiently diffracted by these layers and, being made of carbon, there is relatively small absorption.

Any effective monochromator must be able to diffract a fairly high percentage of the beam incident upon it and a physical description of the scattering process in such a monochromator is unlikely to be given by the kinematic theory which assumes that there will be no significant reduction in the intensity of the main beam as it passes through the crystal. Thus the behaviour of a graphite monochromator can be considered a problem in extinction and Jennings (1981) has examined the applicability of a number of theories of extinction to monochromators, particularly as applied to polarization ratios.

The polarization ratio of a monochromator is the ratio of the intensity diffracted parallel to the diffraction plane to that diffracted perpendicular to the diffraction plane. The appropriate intensity will be either the integrated intensity if the divergence of the incident beam is greater than the rocking curve of the monochromator, the reflected intensity if *vice versa*. Most practical situations will correspond to an intermediate case.

When the beam from a monochromator is itself scattered by a second crystal, it is necessary to know the state of polarization of the beam from the monochromator if the intensity of the beams from the

second crystal are to be correctly related to structure factors. If the scattering in the monochromator obeys the kinematic theory, the polarization ratio will simply be $\cos^2 2\theta_G$, where θ_G is the Bragg angle; if the monochromator is perfect, the polarization ratio will be $\cos 2\theta_G$. However, as has been pointed out by Jennings (1968, 1981), when severe extinction occurs in a mosaic crystal, much of the incident energy of each polarization will be diffracted and the polarization ratio could approach unity.

Le Page, Gabe & Calvert (1979) have described a method of experimentally determining polarization ratios and obtained values greater than $\cos 2\theta_G$ for Cu $K\alpha$ and Mo $K\alpha$ radiations. Using two crystals of differing mosaic spreads, they obtained polarization ratios which were not significantly different. Vincent & Flack (1980), using a method which involved a comparison of data collected with filtered and monochromatized radiation, obtained a value of the polarization ratio between $\cos^2 2\theta_G$ and $\cos 2\theta_G$ for Cu $K\alpha$ radiation, but outside that range for Mo $K\alpha$ and Ag $K\alpha$ radiations. The present study describes the measurement of the reflecting powers and integrated intensities from a graphite monochromator over a range of wavelengths, the comparison of the results with the theory of X-ray diffraction in mosaic crystals of Zachariasen (1945), and the deduction of the corresponding polarization ratios.

Experimental

A graphite monochromating crystal, of thickness 0.922 (3) mm and cross section 20 × 10 mm was mounted on a Siemens four-circle diffractometer, the X-ray tube housing of which had been adapted so that it could rotate about a vertical axis. A second monochromator, a perfect silicon crystal reflecting in the 111 position, was placed over the main-beam outlet port so that a monochromatic beam could be directed onto the graphite. The divergence of the beam from the silicon was 35'' for a characteristic beam and 5' for white radiation. The beam from the silicon was passed through a collimator of width 0.6 mm.

The wavelengths used were the K lines from silver, molybdenum and copper X-ray tubes and samples of the white radiation and some L lines from a tungsten

X-ray tube. Because the beam incident on the graphite was parallel, it was expected that the polarization ratio from the graphite crystal would correspond to the reflectivity polarization.

For each wavelength, the graphite crystal was set so that the maximum reflected intensity for the 002 reflection was recorded and a measurement of the incident beam intensity enabled the maximum reflecting power, R_o , the ratio of the reflected to the incident intensity, to be obtained. The absolute integrated intensity, ρ_o , was also measured, along with the full width at half maximum (FWHM) of the diffraction profile which was found to have a constant value over the wavelength range of 0.26 (1)°. A θ scan of 1° was used which must include a proportion of thermal diffuse scattering which would tend to overestimate ρ_o . The values of R_o and ρ_o are given in Tables 1 and 2 respectively. Sufficient counts were taken to achieve a statistical accuracy of at least 1% in R_o and ρ_o . The reproducibility was better than 2%.

Discussion

Using the Darwin formulism, Zachariassen (1945) determined the scattering from a plane parallel plate diffracting in the symmetrical Bragg position, that is, the situation under which a monochromator operates. The theory is based on the solution of differential equations which represent the variation in the power of both the incident and the diffracted beams as they pass through the crystal and takes into account the energy lost from and gained by the beams due to diffraction. The differential equations can be solved for the symmetrical Bragg case and give a reflecting power, R , by the equation

$$R = \frac{\sigma + \mu/\gamma - u}{\sigma} - \frac{u[\sigma + \mu/\gamma - u] \exp(-ut)}{\sigma[(\sigma + \mu/\gamma) \sinh ut + u \cosh ut]}, \quad (1)$$

where $u = [(\sigma + \mu/\gamma)^2 - \sigma^2]^{1/2}$, σ is the reflectivity per unit length measured along the surface normal of the crystal and is obviously a function of the scattering angle and the diffraction profile, γ is the direction cosine of the incident and diffracted beams relative to the crystal surface, μ is the linear absorption coefficient and t is the crystal thickness. The second term in the equation for R represents that part of the beam which is transmitted through the crystal and, although it was negligible for most wavelengths, was included in the calculations.

If we assume a Gaussian profile, the reflectivity, σ , at a small angle $\Delta\theta$ from the centre of the Bragg peak is given by (Weiss, 1966)

$$\sigma(\Delta\theta) = \frac{Q\sqrt{2g}}{\gamma} \exp[-2\pi(\Delta\theta)^2 g^2], \quad (2)$$

where

$$g = 0.664/\text{FWHM}$$

and

$$Q = \frac{r^2 |F|^2 \lambda^3 K^2}{V^2 \sin 2\theta_G}.$$

K^2 is the polarization and all other symbols have their usual meaning.

The two states of polarization can be considered separately and it will be assumed that the beam from the silicon monochromator has been partially polarized, with the intensities of the parallel and the perpendicular components being in the ratio of $\cos 2\theta_M$ to 1, where θ_M is the Bragg angle of the monochromator. This assumes that the silicon crystal is indeed perfect and the presence in the beam of the essentially kinematic thermal diffuse scattering and contributions from the partially polarized continuum will introduce uncertainties in this ratio. However, it must be emphasized that the results are not sensitive to the polarization of the beam from the silicon monochromator.

Thus, for the parallel component reflected from graphite, the reflectivity at peak centre, $R_{||}$, can be obtained by substituting in (1)

$$\sigma_{||} = Q_{||} \sqrt{2g/\gamma},$$

where

$$Q_{||} = \frac{r^2 |F|^2 \lambda^3 \cos^2 2\theta_G}{V^2 \sin 2\theta_G}.$$

The equivalent perpendicular component, R_{\perp} , is obtained by substituting

$$\sigma_{\perp} = Q_{\perp} \sqrt{2g/\gamma},$$

where

$$Q_{\perp} = \frac{r^2 |F|^2 \lambda^3}{V^2 \sin 2\theta_G}.$$

The resultant reflectivity is, therefore,

$$R = \frac{R_{\perp}}{1 + \cos 2\theta_M} + \frac{R_{||} \cos 2\theta_M}{1 + \cos 2\theta_M}.$$

These values were calculated at each wavelength, the value of the structure factor F being taken to be 16.6 (Kestenbaum, 1973). The absorption coefficients, interpolated where necessary, were those of Berry & Lawrence (1979).

Table 1 shows the $R_{||}$, R_{\perp} and the resulting R values along with the measured R_o values at the wavelengths chosen. Owing to the similarity in the variation with wavelength of both the scattering and the absorption, the R values do not vary much over the wavelength range, rising to a peak value of 0.546 at a wavelength

of about 0.7 Å. The observed R_o values follow approximately the same pattern, having a maximum value at the same wavelength but are on average 4% greater than the corresponding R values. Systematic errors arising from an incorrect assumption regarding the state of polarization of the beam from the silicon crystal and from errors in the structure factor would be insufficient to account totally for this difference. While the theory has limitations, (e.g. no account is taken of coherent scattering effects or of diffraction broadening), it was felt that the agreement was sufficiently close to allow meaningful deductions as to the scattering mechanism to be made.

The reflectivity polarization ratio for the beam scattered by the graphite, P , will be given by the ratio of R_{\parallel} to R_{\perp} . The ratios are listed in Table 1 and in all cases are greater than the corresponding values of $\cos 2\theta_G$ and tend towards unity at lower wavelengths.

The extent to which multiple scattering takes place within the crystal can be envisaged by expanding the equation for R , assuming no transmitted beam, as an infinite series.

$$R = x + x^3 + 2x^5 + 5x^7 + \dots,$$

where

$$x = \frac{\sigma}{2(\mu/\gamma + \sigma)}.$$

The magnitudes of the terms in x , x^3 , x^5 , x^7 , etc. represent the contribution to R from one, three, five, seven, etc. times scattered radiation. The proportions vary very little over the wavelength range, about 80% of the diffracted beam is once scattered, 13% has been scattered three times and even the nine-times-scattered beam contributes about 1% of the total.

A knowledge of the structure factor and the absorption factor enables the calculation of the kinematic integrated intensity, ρ_K , to be made from

$$\rho_K = \frac{r^2 |F|^2 \lambda^3 K^2}{V^2 \sin 2\theta_G} \left[\frac{1 - \exp(-2\mu t \operatorname{cosec} \theta_G)}{2\mu} \right],$$

where

$$K^2 = \frac{1 + \cos 2\theta_M \cos^2 2\theta_G}{1 + \cos 2\theta_G}.$$

Table 2 shows the values of ρ_K with the observed values of ρ_o and it can be seen that the observed values are, on average, less than 40% of the kinematic values, demonstrating that the scattering process cannot be assumed to be kinematic. Kestenbaum (1973) measured integrated intensities at wavelengths above 1.66 Å and obtained integrated intensities approximately two-thirds of their kinematic values with a crystal of FWHM of 0.8°.

Zachariasen's equation for the reflecting power (equation 1) can be integrated numerically over the complete Bragg angle using $\sigma(\Delta\theta)$ given by (2). This was done considering the two polarization states separately giving the integrated intensities ρ_{\perp} and ρ_{\parallel} and the resultant integrated intensity ρ . These are also listed in Table 2. The ρ_o values exceed the ρ values by 10% on average. Also listed in Table 2 are the ratios of the integrated intensities for each polarization.

Table 1. At wavelength λ , R_{\parallel} and R_{\perp} are the reflecting powers for the parallel and perpendicular components of polarization from Zachariasen's equation, R is the resultant reflecting power, R_o is the measured reflecting power and P is the polarization ratio

λ (Å)	R_{\parallel}	R_{\perp}	R	R_o	P
0.497	0.528	0.532	0.530	0.528	0.992
0.561	0.534	0.539	0.537	0.541	0.991
0.594	0.539	0.545	0.542	0.550	0.989
0.632	0.540	0.547	0.544	0.565	0.989
0.671	0.541	0.549	0.545	0.572	0.987
0.710	0.542	0.550	0.546	0.584	0.985
0.780	0.540	0.549	0.545	0.573	0.984
0.853	0.527	0.538	0.533	0.545	0.980
0.902	0.523	0.535	0.529	0.527	0.978
0.968	0.516	0.530	0.523	0.520	0.974
1.030	0.507	0.523	0.515	0.516	0.969
1.096	0.498	0.518	0.508	0.509	0.961
1.162	0.485	0.506	0.496	0.506	0.958
1.213	0.481	0.504	0.493	0.510	0.954
1.290	0.465	0.491	0.479	0.506	0.947
1.394	0.450	0.481	0.471	0.500	0.936
1.481	0.440	0.475	0.459	0.474	0.926
1.542	0.426	0.465	0.447	0.460	0.916

Table 2. At wavelength λ , ρ_K is the kinematic integrated intensity, ρ_{\perp} and ρ_{\parallel} are the integrated intensities for the perpendicular and parallel components of polarization from Zachariasen's equation, ρ is the resultant integrating intensity and ρ_o is the measured integrating intensity

All values of $\rho \times 10^4$. P is the polarization ratio.

λ (Å)	ρ_K	ρ_{\perp}	ρ_{\parallel}	ρ	ρ_o	P
0.497	92.7	35.7	35.4	35.6	37.2	0.992
0.561	99.3	36.3	35.9	36.1	39.5	0.989
0.594	103.7	36.9	36.4	36.7	40.1	0.986
0.632	107.7	37.4	36.6	36.9	40.8	0.979
0.671	108.3	37.3	36.6	37.0	40.9	0.981
0.710	111.3	37.2	36.5	36.9	41.4	0.981
0.780	113.7	37.1	36.3	36.7	39.6	0.978
0.853	109.1	36.0	35.1	35.6	39.0	0.975
0.902	108.9	35.9	34.8	35.4	37.7	0.969
0.968	106.4	35.4	34.1	34.8	36.5	0.963
1.030	102.8	34.7	33.3	34.0	36.2	0.960
1.096	100.2	34.3	32.7	33.5	36.1	0.953
1.162	93.4	33.2	31.4	32.3	35.0	0.946
1.213	91.9	33.0	31.0	32.0	34.7	0.939
1.290	84.9	31.9	29.6	30.8	34.6	0.928
1.394	79.4	31.0	28.4	29.8	32.4	0.916
1.481	76.0	30.5	27.6	29.2	32.0	0.905
1.542	71.3	29.7	26.5	28.2	31.0	0.892

There have been few direct experimental measurements of the polarization ratio and comparison of results with theory require a knowledge of the mosaic spread of the crystal. Le Page, Gabe & Calvert (1979) have measured the polarization ratios of two graphite crystals, of FWHM 0.42 and 0.60°. A comparison of these experimental results and those obtained using Zachariasen's equations for both the reflectivity polarization ratio and the integrated polarization ratio is shown in Table 3. For Mo $K\alpha$ radiation, there is no significant difference between the experimental results and the calculated ratios while for Cu $K\alpha$ radiation, the measured values agree very well with the reflectivity polarizations for both crystals.

Direct comparison with other measured values of polarization ratio was not possible since in other cases no mosaic spread was quoted. While the value of 0.916 (9) obtained by Vincent & Flack (1980) is consistent with a crystal of mosaic spread 0.3°, assuming the reflectivity polarization ratio is appropriate, the values they obtained for Mo $K\alpha$ and Ag $K\alpha$ radiations cannot be accounted for by any realistic assumption as to the mosaic spread of their crystal.

Conclusions

It has been shown that a pyrolytic graphite crystal conforms closely to the mosaic crystal model and that X-ray scattering in graphite can be described by the Zachariasen solution to the Darwin formulism. This is essentially a theory of extinction since it takes into account the variation in the intensity of the main beam as it passes through the crystal and, unlike theories of extinction based on Zachariasen (1967), it deals adequately with the absorption effects which are significant in large crystals.

The scattering can be simply described. The perpendicularly polarized component undergoes multiple scattering within the crystal and the magnitude of the emergent radiation depends on the efficiency of the scattering and on the absorption. The efficiency of scattering of the parallel components of polarization is less than that of the perpendicular components (by a factor of $\cos^2 2\theta_G$) and thus relatively more absorption

Table 3. Comparison of the reflectivity polarization ratio $P(z)$, and the integrated polarization ratio $P'(z)$ with the experimental values of Le Page, Gabe & Calvert (1979), $P(\text{LGC})$, for Mo $K\alpha$ and Cu $K\alpha$ radiations

	Mo $K\alpha$ radiation		Cu $K\alpha$ radiation	
FWHM	0.42°	0.60°	0.42°	0.60°
$P(Z)$	0.983	0.980	0.901	0.888
$P'(Z)$	0.980	0.976	0.880	0.867
$P(\text{LGC})$	0.973 (5)	0.970 (3)	0.908 (6)	0.897 (6)

Table 4. Variation of FWHM of the diffraction profile with reflectivity R , the integrated intensity ρ , the reflectivity polarization P and the integrated polarization P' for Cu $K\alpha$ radiation

FWHM (°)	R	$\rho (\times 10^4)$	P	P'
0.1	0.601	15.8	0.946	0.927
0.2	0.490	24.3	0.927	0.902
0.3	0.422	30.2	0.912	0.888
0.4	0.372	34.5	0.903	0.880
0.5	0.335	38.0	0.895	0.872
0.6	0.305	40.7	0.888	0.867
0.7	0.280	43.0	0.882	0.861
0.8	0.259	44.9	0.877	0.857
0.9	0.242	46.5	0.872	0.854
1.0	0.226	47.6	0.868	0.852

takes place. In the limit of an infinitely thick crystal of zero absorption, both polarizations would be completely reflected, giving a polarization ratio of unity.

The reflecting powers quoted here give a measure of the efficiency of graphite as a monochromating crystal and show that, for a FWHM of 0.26°, 58 and 46% of beams Mo $K\alpha$ and Cu $K\alpha$ are reflected. The theory predicts that the reflection coefficient and, thus, the integrated intensity, will be dependent on the mosaic spread of the graphite and in Table 4 are listed the reflection coefficients and the integrated intensities for FWHM values of 0.1 to 1.0°, assuming an unpolarized incident beam of Cu $K\alpha$ radiation. The reflected and integrated polarization ratios are also listed. The decrease in the reflection coefficient with increasing mosaic spread demonstrates the fall in the efficiency of the scattering (the number of blocks) at the centre of the rocking curve – the increase in the integrated intensity demonstrates the more kinematic nature of the scattering for the wider distribution of blocks. Both polarization ratios decrease with increasing mosaic spreads because of the fall in the efficiency of the scattering, the integrated polarization ratio being the smaller since the scattering away from peak centre is more kinematic than at peak centre. Both ratios are tending towards $\cos^2 2\theta_G$.

While it may be tempting to calculate a polarization ratio of a graphite crystal using this theory it must be remembered that, although the polarization ratios seem to be in agreement with experimental values, discrepancies do exist between the theory and the measured intensity values presented here. The advice of Jennings (1968, 1981) to measure the polarization ratio should be considered.

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Crystal Powder Statistics.

IV. Calculation of the Line Profile Using the Sampling-Line Method

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(Received 30 November 1981; accepted 23 June 1982)

Abstract

The sampling-line method is a convenient procedure for evaluating the line profile of a polycrystalline sample. To deal with size-broadening effects only, the method is applied to Bernoullian and Gaussian samples; the line profile is given by a Lorentzian function in the first case and by a similar function in the second case. For *any real* polycrystalline sample the intensity decreases as s^{-2} for large $|s| = |S - S_{hkl}|$. For a given average thickness the apparent crystallite size is up to 2 times larger than for samples consisting of crystals with the same size and shape.

Introduction

The influence of crystal size distributions on diffraction profiles is an important subject at present, in that an accurate knowledge of the line shape is required for the structural refinement *via* powder analysis, such as the Rietveld method (*e.g.* Albinati & Willis, 1982).

Following previous studies on the subject (Allegra, Bassi & Meille, 1978; Allegra & Ronca, 1978, 1979), in the present paper we will propose a general mathematical treatment for simple statistical distributions. A few examples of line profiles thus obtained will be compared with well-known results from single crystals (see, in particular, Wilson, 1949), with the purpose of providing simple guidelines for the characterization of the sample statistics.

We shall confine our attention to those crystal size distributions that may be factorized into terms each depending on a single crystallite thickness. In other words, if the crystals are bound by n sets of planes and $d_i (i = 1, \dots, n)$ is the distance between two consecutive

parallel planes of the i th set for the general crystal, we have

$$p(d_1 d_2 \dots d_n) = p(d_1) p(d_2) \dots p(d_n), \quad (1)$$

where the p 's are normalized probability density functions. The theory will be applied to the Bernoullian and Gaussian distributions, already considered in previous papers. For the former case (Allegra, Bassi & Meille, 1978), the present treatment may be viewed as an extension of the results to the general model with any number of boundary planes. For the Gaussian distribution, an error contained in the former approach (Allegra & Ronca, 1978) was pointed out later (Allegra & Ronca, 1979), but its consequences on the results were not amended, so that they are only correct for particular classes of reflections; the procedure given in this paper leads to the general result.

The method of the sampling line

Stokes & Wilson (1944) showed that the size-dependent line profile is uniquely related with the probability distribution of the lengths of the intra-crystalline chords parallel to $\mathbf{S}_0 = \mathbf{S}(hkl)$ ($S = |\mathbf{S}| = 2 \sin \theta / \lambda$; a chord is defined as any segment having both ends on the crystal surface). Indicating by T the general chord length and by $p(T)$ its area probability density, we derive the general expression of the line profile for any polycrystalline specimen from that proposed for identical crystals (*cf.* Wilson, 1949, ch.IV, equation 5) as

$$\mathcal{F}(s) = \mathcal{N}/V \int_0^\infty p(T) \frac{\sin^2(\pi Ts)}{(\pi s)^2} dT / \langle T \rangle, \quad (2)$$

where s is the difference $S - S_0$ between the general value of S and that corresponding to the hkl point in