Analysis of Two-Dimensional Reflections from a Fine-Particle Carbon

BY R. CAMINITI, G. LICHERI, G. PICCALUGA* AND L. SCHIFFINI†

Istituto Chimico Policattedra, Università di Cagliari, Via Ospedale 72, 09100 Cagliari, Italy

(Received 12 February 1979; accepted 27 July 1979)

Abstract

The intensities of two-dimensional reflections from a non-graphitic carbon were correctly calculated by using the general Debye scattering equation and the hypothesis of small (about 12 Å in diameter) domains diffracting incoherently with respect to one another.

The so-called non-graphitic carbons are examples of a turbostratic structure in which parallel graphite layers have random orientations about the normal to the layers. The X-ray diffraction pattern from such material shows the three-dimensional lattice reflections 00l and the two-dimensional lattice reflections hk.

Starting from the work of Warren (1941), many attempts have been made to evaluate either the profiles of single reflections (00l or hhk) or a wider part of the experimental diffraction pattern. Most of the early works (Franklin, 1950; Alexander & Sommer, 1956; Diamond, 1957, 1958; Doi, 1961) were based on the hypothesis that the shapes and the widths of the reflections were determined essentially by the particle sizes of the carbons (that is, the graphitic layer dimension in the case of hhk reflections and the parallel layer group dimension normal to the layers in the case of 00l reflections). Therefore, one of the aims of these works was the evaluation of these dimension parameters.

Within these general lines a very interesting suggestion was put forward by Diamond (1957) who proposed calculating the diffraction intensities from the hhk reflections by using the general Debye scattering equation:

\[ i(s) = \frac{I(s)}{f^2(s)} - 1 = \sum_r n(r) \frac{(\sin sr)}{sr} , \]

where \( i(s) \) = reduced intensity function; \( s = 4\pi \sin \theta / \lambda \) (2θ being the scattering angle and \( \lambda \) the X-ray wavelength); \( f(s) \) = atomic scattering factor; \( I(s) \) = coherent diffraction intensity per atom in electron units; \( n(r) \) is the number of interatomic vectors of length \( r \) within the layer. In a layer of infinite extent, \( n(r) \) is simply the number of atoms at a distance \( r \) from any atom. For a lattice of finite extent \( n(r) \) must be modified in order to account for the reduction of the coordination as \( r \) increases.

Diamond (1957) determined empirically the factor \( n(r) \) by considering aromatic molecules of arbitrary shape and particular size range as a model for the graphitic layers of real carbons.

Diamond himself (1958) showed that, when making comparisons with experimental data, it could be important to consider the possible distribution of layer sizes around an average value and proposed a method of fitting the synthetic hhk intensity functions to the observed intensities, which in turn should give a layer size distribution as a direct result.

Later, Warren & Bodenstein (1965) extended Diamond's treatment to include the interaction between the different layers in a parallel layer group so that 00l reflections could also be evaluated. The combination of these approaches, in principle, allows the computation, through Debye's equation, of the entire diffraction pattern. However, the use of these methods has been very limited because of the considerable practical difficulties. In fact, it is not easy to account for the particle size distribution; furthermore, for sizes large enough (> 50 Å), the summations in Debye's equation must include too many terms. Therefore, only applications limited to restricted parts of the spectrum or to single reflections (for example 110 or 100 reflections) have usually been carried out.

Investigating a commercial carbon used as support material for metallic catalysts, we met a case where the use of Diamond's treatment came out particularly simply. In fact, this carbon gave rise to an extremely diffuse diffraction pattern, very similar to the ones characteristic of amorphous or liquid samples. In the reduced intensity function given in Fig. 1, only the 002 peak was evident besides the hhk peaks; however, it was so clearly discernible from the others, that we could tentatively analyse the intensity function for \( s > 2 \text{ Å}^{-1} \) using Debye's equation in order to evaluate only the contributions within the graphitic layers. Intensity data were collected with a \( \theta-2\theta \) GSD Seifert diffractometer which uses parafocusing geometry; the instrument provides for a simultaneous angular motion of the X-ray tube and the detector about a horizontal axis lying on the sample surface. Monochromatic Mo K\( \alpha \) radiation was obtained by reflection from a curved quartz crystal mounted in the diffracted beam.

Scattering intensities were collected at discrete points from \( \theta = 2 \) to \( \theta = 55^\circ \), corresponding to the range 0.65
<s<14.47 Å⁻¹. Times required to accumulate at least 100000 counts at each angle were recorded. The measured intensities were corrected for background, polarization and absorption (Milberg, 1958). In order to correct the data for Compton radiation, the independent scattering was measured at high angle and then the Compton contribution was empirically evaluated over the whole angular range in order to account for monochromator discrimination (Levy, Danford & Narten, 1966). The corrected intensities were scaled to the independent scattering factor using both the analytical method (Krogh-Moe, 1956) and visual comparison. The values of the scattering factors were calculated according to Hajdu (1972). A correction for residual systematic errors in the reduced intensity function i(s) was also applied (Levy, Danford & Narten, 1966).

Useful suggestions for the analysis of intensity data were drawn by examining the radial distribution curve of the sample, obtained by Fourier transforming the experimental reduced intensity function. In fact, the radial curve, given in Fig. 2, not only exhibited its maxima in correspondence to the interatomic distances typical of a graphitic structure, but it also clearly pointed out that deviations of the radial density from the average one (the so-called order range) were meaningful only up to about 12 Å. We then assumed this value as representing the size of the layers and tried a computation of the intensity function by introducing into Debye's formula the n(r) coefficient assigned by Diamond to molecules of nominal diameter equal to 12 Å (clearly it does not mean that the material here considered is composed of small independent particles 12 Å in size, but that 12 Å is the size of the domains or crystallites coherently scattering). Furthermore, since the diffraction pattern was extremely diffuse, we believed that an important component of the line broadening should be ascribed to lattice disorder. In order to account for this effect we introduced in (1) a gaussian-type strain function, exp [−½σ²(r)r²], where σ(r) is the mean square deviation for each distance r. In this way the expression of the synthetic i(s) function became formally equal to the one we used when analyzing X-ray diffraction data of liquids and solutions, which seemed reasonable considering the amorphous-type diffraction pattern obtained in this case. However, the procedure of fitting the synthetic intensity function to the experimental one was here extremely easy and fast, in that the number of adjustable parameters was limited to two, the first neighbour C-C distance and one mean square deviation. In fact, if one assumes that the graphitic layers have a benzenoid (that is, completely resonant) structure, all the interatomic distances may be calculated when fixing the first one; also, since the peaks in the radial distribution curve have an almost constant width, the same mean square deviation can be reasonably assumed for all the interatomic distances. It is worth noting that the coefficients n(r) have not been treated as independent parameters, as their values come out from the order range deducible from the experimental radial distribution function.

The synthetic structure function thus calculated appeared in fairly good agreement with the experimental data on the entire angular range explored (except, obviously, the 002 peak and the small-angle region). This can be observed in Fig. 1 where the theoretical i(s) function is shown as a solid line against experimental data (circles). The final values of the independent parameters were r<sub>C</sub> = 1.424 Å and σ = 0.084 Å.

The agreement between theoretical and experimental functions can be regarded as qualitatively good, especially if one considers that all the hk peaks measured experimentally are reconstructed with remarkable accuracy. Obviously, analyses restricted to smaller parts of the spectrum could give even better agreements with the experimental functions in the regions considered, but it would be questionable
whether these results would provide more reliable information as they could come from more flexible adjustments of the theoretical curves to the experimental one. For example, Ergun & Schehl (1973) noticed that 'varying layer sizes are obtained from different hk reflections'.

In any case, in our opinion, the agreement between model and experimental data can be further improved. In fact, the simplicity of the procedure used here was achieved by introducing the following approximations: (a) one fixed size for the graphitic layers has been assumed, rather than a distribution of sizes; (b) the contributions from the 00l reflections have been omitted; they would probably influence the experimental hk profiles with fringes, even if no distinct peak is observable (apart from the 002 reflection); (c) the contribution from reticular strain has been oversimplified; (d) any possible presence of C atoms (among the domains coherently scattering) disorganized or connected by means of a random network has been neglected. Inaccuracy could also result from the use of scattering factors (Hajdu, 1972) which may not be able to describe properly the C atoms in the sample investigated, while not having considered the possible presence of a quinoid structure in the graphitic layers should turn out to be of minor importance, as demonstrated by Ergun & Schehl (1973). However, considering the satisfactory reproduction of the whole hk spectrum instead of single reflections, it is difficult to suspect that the approximations counterbalance each other; this therefore indicates that the approximations are not too important and suggests that the shape of the diffraction pattern can be explained by the effect we have dealt with, that is, interactions among C atoms arranged in layers of graphite type of somewhat reduced sizes. Anyhow, it is our intention to consider in detail the other possible contributions to the peak profiles. In addition to the problems mentioned above, attention should also be devoted to studying treatments different from the one proposed by Diamond (1957) in order to account for the reduction of the n(r) coefficients, in comparison with the values they assume in the case of infinite graphitic layers. In fact, Ergun (1970) affirmed that in amorphous carbons the broadening of diffraction lines (in addition to important strain effects) is due to the existence of large but defective domains rather than small domains diffracting incoherently with respect to one another. On these grounds he proposed an n(r) factor essentially different from the one used in the present work and tested it in a deep analysis of the structure of a glassy carbon. Therefore, the adaptability of Ergun's treatment to our data will be considered in the future.

We are very grateful to Professor C. Dejak and Dr G. Cocco for many helpful discussions. This work was partially supported by the Consiglio Nazionale delle Ricerche. All the calculations were performed at the Centro di Calcolo Elettronico, University of Cagliari.

References