International Atomic Energy Agency

and

United Nations Educational Scientific and Cultural Organization

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

RADIAL DISTRIBUTION ANALYSIS OF AMORPHOUS CARBON *

C^{14}

C.A. Majid

International Centre for Theoretical Physics, Trieste, Italy,

and

Pakistan Institute of Nuclear Science and Technology, P.O. Nilore,

Rawalpindi, Pakistan. **

ABSTRACT

The radial distribution analysis of amorphous carbon
obtained from graphite is discussed. The various interatomic distances
obtained were 1.44 Å, 2.57 Å and 3.2 Å. The coordination numbers for
the first, second and third coordination sphere for this form of amorphous
carbon were noted to be 3.15, 10.7 and 15.5, respectively. Values of
the interatomic distances and the coordination numbers were found to lie
between those for graphite and diamond.

MIRAMARE – TRIESTE

September 1982

* To be submitted for publication.

** Permanent address.

---

1.   INTRODUCTION

For the last two decades there has been much interest
in studies of the structural and other properties of amorphous solids.
In particular carbon has attracted the attention of scientists
interested in its structure – property relations. Because of its
increasing use, structural studies of carbon in its various forms –,
particularly the amorphous form, are becoming increasingly important.

Amorphous solids possess a "frozen – in" liquid
structure: the atomic arrangements in these solids are not spatially
periodic. Their X – ray diffraction patterns consist of one or more
broad and diffuse rings (halos). Sharp lines characteristic of long
range order are not present. Characterization of these materials is
carried out in terms of a radial distribution function (RDF) which
determines the number of atoms surrounding a given atom i.e. the
' coordination number ' at a given radial distance from the given atom.
The position of the peak in the radial distribution curve gives the
most probable interatomic distance between a pair of atoms, and its area
the coordination number. The coordination number can be compared with
a given model and hence the most probable arrangement of atoms in the
sample under study can be inferred. The advantage of this method is
that a comparison of different models is possible.

The X – ray diffraction patterns of all types of
amorphous carbon studied sofar show two broad halos in the approximate
neighbourhood of diffraction angles corresponding to the 002 and 100
planes of graphite. This led the early workers (1-7) to assume that
amorphous carbon consisted of very small particles of graphite so
arranged that only the 002 and 100 reflections remained intact, while
the remaining peaks cancelling out. Although some authors observed
additional peaks, the concept of the defective graphite crystallite as
the basic model remained intact, the model being continually refined
(7-20) to accomodate the experimentally observed information.

Nelson (6) was the first to apply the technique of
radial distribution analysis developed by Warren and Gingrich (21) to
the analysis of carbon structure. Warren and Mozzi (22) improved this
method further. The present analysis of the structure of amorphous
carbon is based on the technique described by Warren (23).

In the past, X – ray diffraction patterns of amorphous carbon have generally been recorded using the film technique of Debye – Scherrer (1-7, 4-28). Because of several limitations this method is not likely to furnish data of high accuracy as with modern diffractometers (28). Recently Sanyal et al (29) have reported radial distribution analyses of amorphous carbon samples obtained from the pyrolysis of benzene, sucrose and toluene, etc., using an X – ray diffractometer. These authors employed Ni – filtered Cu – Kα radiation. Cu – Kα radiation allows one to record diffraction patterns only up to K (= $4\pi \sin\theta / \lambda$) equal to about at the most 8 Å, whereas the radial distribution analysis demands the diffraction patterns be recorded for as high a value of K as possible (23,28). Also the diffraction patterns of various carbon samples reported by Sanyal et al (29) appear to show narrow bands superposed upon the broad halos[*]. Their values of the coordination numbers and interatomic distance differ significantly from other authors (25-28) and even in their own work, from sample to sample. This is shown by the results listed in Table 1. They attribute these descrepencies to the structure of the parent material which in their opinion plays a vital role in determining the structure of carbon black. Their radial distribution curves are also different from those reported by various other workers (24-28). The value of the samples used to compute the RDF – curves is not given in Sanyal et al (29).

Inspite of all the efforts made sofar, the interpretation of the amorphous carbon structure still remains controversial. This element crystallizes both with tetrahedral symmetry (diamond) and with layer structure (graphite). The radial distribution function shows the nearest neighbour distance to lie between 1.54 Å (for diamond) and 1.41 Å (for graphite). The area under the first peak yields a first coordination number between 3 (for graphite) and 4 (for diamond). This indicates that the material is an intricate mixture, at the atomic level, of two coordination types. Warren (25-26) explained his results in terms of single graphite layers existing in the sample. Boiko et al (31) claimed that their vacuum – deposited films had a disordered structure similar to that of graphite. Kakinoki et al (32) on the other hand

---

[*] These features tend to suggest that their samples were not completely amorphous, having a comparatively higher degree of structural order in the lattice (30).

claim their samples to be 50 at % diamond – like. It should be noted that the maximum at 1.2 Å^{-1} reported by these authors does not correspond to any graphite or diamond peak and cannot be explained in terms of either structural model (16). ESR and Raman spectroscopy studies made on amorphous carbon films do not support the possibility of " diamond – like " 4 – fold coordination (33).

Stenhouse et al (16) have dealt with the problem theoretically. They suggest that a simple modelling of the RDF for amorphous carbon is not possible. There are at least two forms of bonding analogous to graphite and diamond (16).

In the present paper, we present information on the structure of amorphous carbon obtained from a different source (graphite) and using a modern coputer controlled X – ray diffractometer. To the author's knowledge no such studies are reported on amorphous carbon samples obtained from graphite.

2. EXPERIMENTAL

Samples of amorphous carbon used in these studies were obtained from the PCSIR – Laboratories, Karachi, and were prepared by melting the graphite powder. These samples were a deep black with a bright shining glass – like appearance and were in the form of ingots. They were ground to a grain size of about 5 μm. Purity of the samples was determined from an X – ray flourescence analysis. They were found to be about 99.97 at % carbon, with a total metallic impurity content not more than 100 ppm. The main impurities in the order of decreasing concentration, were Fe, Ni, Zn, Mn, and Cr. The samples were completely amorphous any crystalline content lying below the resolution of the X – ray diffraction technique. The density of this form of carbon was measured to be 2.23 $\pm$ 0.02 gm. cm^{-3}.

The X – ray diffraction patterns were recorded using a computer controlled X – ray diffractometer. Cu – Kα (λ = 1.5418 Å) and Mo – Kα (λ = 0.711 Å) radiation monochromatized by a graphite crystal monochromator placed in the path of the diffracted beam, was used. The final experimental intensity scattering curve was obtained by combining the measurements made with Cu – Kα and Mo – Kα radiation. Intensities were recorded at 0.1 2θ using a NaI detector. The counting time used was 40 sec. at each step. The number of counts recorded

was large enough that the statistical error was less than 1.0 at %. The experimental intensities were corrected for air scattering, the polarization of the X – rays and absorption in the specimen according to the procedure described by Klug and Alexander (28).

To obtain the independent scattering curve for carbon, values of the atomic scattering factors and incoherent factors were obtained from the International Tables for Crystallography, Volume IV (Kynoch Press, Birmingham, 1974). To normalize the experimental intensities to electron units, the corrected Mo – $K\alpha$ intensities were first fitted to the total independent scattering curve at large values of K. Hence the entire Mo–$K\alpha$ intensity curve could be normalized to electron units. The Mo – $K\alpha$ data was then plotted and compared with the Cu – $K\alpha$ intensity data curve for the purpose of normalizing the Cu – $K\alpha$ data to electron units. The contribution of the multiple scattering to the intensities was deduced following the method of Warren and Mozzi (22).

For a flat diffractometer sample the diffracted intensity is given by (23)

$$I_{e.u.} = Hr^2 + Hr^2 \int_0^\infty 4\pi r^2 (\rho(r) - \rho_o) \frac{\sin Kr}{Kr} dr + \frac{(\rho_o f \lambda R)^2}{4(\mu^2 + K^2 \sin^2\theta)}$$

(1)

with

$$H = A\rho_o / 2\mu$$

where A is the area of cross-section of the X – ray beam, ρ_o is the number of atoms per unit volume, R is the radius of the focussing circle and μ is the absorption coefficient. f is the atomic scattering factor.

By subtracting the contribution of the third term for the small – angle region and using the inversion relations of the Fourier integral, the radial distribution function can be expressed as (23)

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_o + \frac{2 r}{\pi} \int K i(K) \sin Kr \, dK$$

(2)

where

$$i(K) = \frac{(I_{e.u.}(K)/N) - f^2}{f^2}$$

(3)

The term $4\pi r^2 \rho(r)$ is the radial distribution function which gives the number of atoms lying between shells of radius r and r+dr with respect to an atom at the origin. Introducing a temperature factor

$e^{-\alpha^2 K^2}$ to suppress the spurious ripples due to truncation of the integration at finite value of K_{max} (the maximum value of K for which experimental observations were possible) equation (2) becomes

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_o + \frac{2 r}{\pi} \int K i(K) \sin Kr \, e^{-\alpha^2 K^2} dK$$

(4)

with

$$\alpha = 1/K_{max}$$

and

$$K_{max} = 17.4 \, \overset{o}{A}^{-1}$$

For evaluating the integral of equation (4) we used a step in K of 0.05.

3. RESULTS AND DISCUSSIONS

Results of these investigations are shown in Figures 1 to 3. Fig. 1 shows the X – ray scattering curve(curve A) in electron units, obtained by combining the results of Cu – $K\alpha$ and Mo – $K\alpha$ radiations. In this figure curve A is compared to the theoretical independent scattering curve for carbon, coherent(curve D), incoherent (curve C) and coherent plus incoherent(curve B) scattering. In Fig.2 the experimental amplitude function Ki(K) is plotted as a function of K. Fig.3 shows the radial distribution function for the samples of amorphous carbon currently being studied. The RDF shows only three well defined peaks. There are however, two more very broad and diffuse peaks centred arround 4.4 $\overset{o}{A}$ and 5 $\overset{o}{A}$. The dotted line in Fig. 3 is the $4\pi r^2 \rho_o$ – curve. The interatomic distances and coordination numbers obtained from these studies are listed in Table 1. These are compared with the results reported by Sanyal et al(29). The small peak below 1 $\overset{o}{A}$ region in Fig.3 is due to termination errors.

The present studies indicate an average of 3.15 nearest neighbours at a distance of 1.44 $\overset{o}{A}$, 10.7 second neighbours at about 5.57 $\overset{o}{A}$ and 16.5 third neighbours at about 3.8 $\overset{o}{A}$. The first interatomic distance as obtained from the present investigations, lies between that of the three nearest neighbours in graphite (1.41 $\overset{o}{A}$) and the four nearest neighbours in diamond(1.54 $\overset{o}{A}$). This suggests the presence of some diamond – type links; indeed the first and second coordination spheres have coordination numbers (3.15, 10.7) which lie between those of graphite (3, 6) and those of diamond (4, 12). Therefore, the structure of amorphous carbon samples under present studies cannot be explained simply as graphite – like layers, as suggested by Warren (25, 26) and Boiko et al(31) for carbon black. Our results also differ significantly from those of Sanyal et al(29). We did not observe the

peak in the RDF – curve describing the double – bond distance observed by Sanyal et al(29). Also we did not observe a band at $\sin\theta/\lambda = 0.07$ A^{-1} in the experimental intensity curve.

We believe that these structural studies are an important determinant of the detailed behaviour of amorphous carbon.

ACKNOWLEDGEMENTS

REFERENCES

1. G. Asahara, Jap. J. Chem. 1 (1922) 35.
2. C. Mahadeven, Indian J. Phys. 4 (1929) 79.
3. R. Siever, 2nd Conf. on Origion and Consitution of Coal, Nova Scotia (1952) p.341.
4. G. B. Mitra, Acta Cryst. 6 (1953) 101.
5. H. E. Blayden, J. Gibson and H. L. Riley, Proc. Conf. Ultrafine Coals and Coaks, vol.176(1964) 231 (London: British Coal Utilization Research Association).
6. J. B. Nelson, Fuel, 33 (1954) 381.
7. P. B. Hirsch, Proc. R. Soc. London, 226(1954) 143.
8. R. E. Franklin, Acta Cryst. 3 (1950) 107.
9. A. J. C. Wilson, Acta Cryst. 2 (1949) 245.
10. R. Diamond, Acta Cryst. 10 (1957) 359.
11. J. Mering and J. Maire, J. Chem. Phys. 57(1960) 803.
12. W. Rudland, Carbon 2 (1965) 365.
13. L. Paulin, Proc. Nat. Acad. Sci. USA, 56 (1966) 1646.
14. B. E. Warren and Bodenstein, Acta Cryst. 20 (1966) 602.
15. S. Ergun and T. J. Gifford, J. Appl. Cryst., 1 (1968) 313.
16. B. J. Stenhouse and P. J. Grout, J. Non-cryst. Sol., 27 no. 2 (1978) 247.
17. B. J. Stenhouse, P. J. Grout, N. H. March and J. Wenzel, Phil. Mag., 36 no. 1 (1977) 129.

18. P. H. Gaskell and A. Howie, in: Physics of Semiconductors, Ed.: M. H. Pilkuhan (Teuber, Stuttgart, 1974) p.1076.
19. P. H. Gaskell, Phil. Mag., 32 (1975) 211.
20. O. L. Krivanek, P. H. Gaskell and A. Howie, Nature, 262, August 5 (1976) 454.
21. B. E. Warren and N. S. Gingrich, Phys. Rev., 46 (1934) 368.
22. B. E. Warren and R. L. Mozzi, Acta Cryst., 21 (1966) 459.
23. B. E. Warren, X – ray Diffraction (Addison Wesley, Reading, Massachussett, 1969).
24. P. K. Sharivastawa and S. C. Sen, Proc. Symp. on Non – crystalline Solids, Kanpur, India (1980) p.33.
25. B. E. Warren, Phys. Rev., 59 (1941) 693.
26. B. E. Warren, J. Chem. Phys., 2 (1934) 551.
27. R. P. Messmer and J. Wong, J. Non-cryst. Sol., 45 (1981) 1.
28. H. P. Klug and L. E. Alexander, X – ray Diffraction Procedures for Polycrystalline and Amorphous Materials(Wiley,New York,1974).
29. S. K. Sanyal, B. K. Samantaray and G. B. Mitra, Acta Cryst. A38 (1982) 333.
30. C. A. Majid, P. R. Prager, N. H. Fletcher and J. M. Brettell, J. Non-cryst. Sol., 16 (1974) 365.
31. B. T. Boiko, L. S. Palatnik, A. S. Derevyanchenko and Y. M. Voronin, Rev. Roumaine Phys., 13 (1968) 767.
32. J. Kakinoki, K. Katada, T. Hanawa and T. Ino, Acta Cryst. A13 (1960) 171.
33. N. Wada, P. J. Gaczi and S. A. Solin, J. Non-cryst. Sol., 35-36 (1980) 543.

FIGURE CAPTIONS

Fig. 1: X - ray scattering curves for amorphous carbon:
A— An X - ray scattering curve in electron units
B— Total independent scattering curve (C + D)
C— Incoherent scattering curve
D— Independent scattering curve (coherent, f^2)

Fig. 2: Plot of the experimental amplitude function Ki(K) for amorphous carbon.

Fig. 3: Radial distribution function(RDF) of amorphous carbon. Peak positions are listed on top of peaks.

TABLE 1

Peak positions and coordination numbers for amorphous carbon as obtained from present studies and those reported in Sanyal et al. (29) for different carbon black samples obtained from: (A) ultracarbon, (B) benzene, (C) sucrose, (D) toluene.

PEAK NO.	Peak positions								Coordination numbers					
	1	2	3	4	5	6	7	8	1	2	3	4	5	6
This work	1.44	2.57	3.8						3.15	10.7	16.5			
A	1.45	2.3	3.1	3.95	4.7	5.5	6.4	7.2	4.3	5.8	11.0	15.0	—	—
B	1.4	2.35	3.2	4.0	4.8	5.6	6.45	7.2	-.2	6.8	10.4	16.0	—	—
C	1.35	2.48	3.15	3.8	4.75	5.75	6.6	7.5	2.4	4.8	4.4	13.0	—	—
D	1.3	2.25	3.1	4.05	4.95	5.85	6.75	7.8	2.7	5.6	11.2	16.6	—	—

Fig.1

Fig.2

Fig.3