XRay Diffraction Study of Carbon Black

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X-ray diffraction patterns of carbon black have been made with strictly monochromatic radiation. Without making any assumptions as to the crystallinity of the material, the distribution of atoms about any one atom has been determined directly from the experimental scattering curve by the method of Fourier integral analysis. The results indicate definitely the existence of single graphite layers. Whether these layers have definite orientation and position with respect to one another (graphite crystal) or whether carbon black is a mesomorphic form of carbon, cannot be definitely decided from the experimental results. It is probable that carbon black is a heterogeneous mixture of particles which range from single graphite layers up to graphite crystals several layers thick. The intense small angle scattering is due to the difference between grain density and average density, caused by the loose packing of the extremely small grains.

INTRODUCTION

X-RAY diffraction studies of carbon black have been reported by a number of workers.[1] In most cases a pattern was obtained which comprised two or three broad diffuse rings, the rings having roughly the same position as the strongest lines in the powder pattern of graphite. A number of workers have concluded from this fact alone that carbon black is simply a fine grained form of crystalline graphite. However, since the appearance of the pattern is very similar to that of a typical liquid or amorphous solid, this immediate conclusion does not seem justified. In order to get as much information as possible from the diffraction pattern without making any *a priori* assumptions as to the crystallinity of the material, the scattering curve has been interpreted in the present work by the more powerful method of Fourier integral analysis. By this method, one obtains directly from the experimental scattering curve, the distribution of atoms about any one atom, regardless of whether the material is crystalline or amorphous.

EXPERIMENTAL

In order to eliminate the extraneous background blackening, it is necessary to use a strictly monochromatic beam and to evacuate the camera to avoid air scattering. The radiation from a copper target Müller tube was monochromatized by reflection from a rocksalt crystal and the cylindrical camera was evacuated during the exposure. The details of the experi-

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[1] (a) Ewald and Hermann, Strukturbericht, 1913–1928: (b) G. L. Clark, Coll. Sym. Mon. **4**, 155 (1926): (c) P. Krishnamurti, Ind. J. Phys. **5**, 473 (1930): (d) U. Hofmann, Zeits. angew Chem. **44**, 841 (1931): U. Hofmann and D. Wilm, Zeits. f. physik. Chemie **B18**, 401 (1932): (e) C. Mongan, Hel. Phys. Acta **5**, 341 (1932): (f) F. Trendelenburg, Hel. Phys. Acta **6**, 477 (1933); Naturwiss. **20**, 655 (1932); Zeits. f. tech. Physik **14**, 489 (1933): (g) Berl, Andress, Reinhardt and Herbert, Zeits. f. physik. Chemie **A158**, 273 (1932): (h) S. B. Hendricks, Zeits. Krist. **83**, 503 (1932): (i) P. C. Mukherjee, Zeits. f. Physik **88**, 247 (1934).
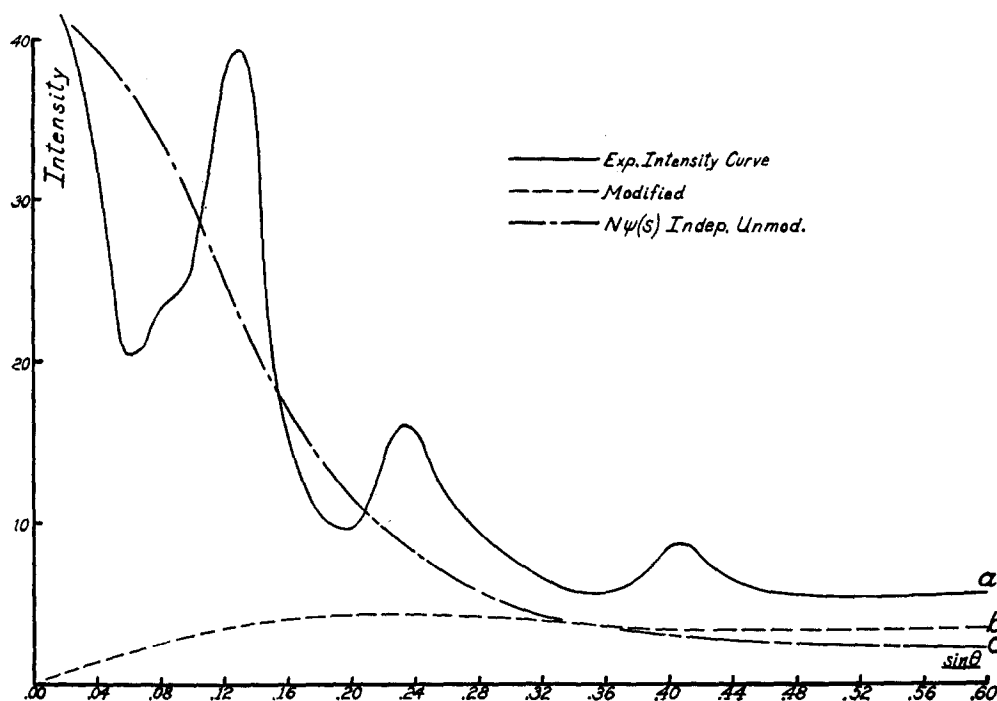
FIG. 1 (a) Experimental intensity curve for carbon black corrected for absorption in sample. (b) Intensity of modified scattering. (c) Independent unmodified scattering.

mental arrangement have been described in a previous paper.[2]

The material used was the commercial carbon black of the Cabot Carbon Co. The material was packed into a small cylinder of cigarette paper of diameter 1.6 mm. With the tube running at 15 m.a. and 30 kv peak, an exposure of 20 hours was sufficient. The microphotometer record of the film was changed into an intensity curve in the usual way. Fig. 1a shows the experimental intensity curve corrected for absorption in the cylindrical sample.[3]

Method of Fourier integral analysis[4]

We assume that in carbon black each atom is surrounded in the same way as every other atom.* Introducing a density function $\rho(r)$ such that $4\pi r^2 \rho(r)dr$ gives the number of atoms between r and $r+dr$ from any given atom, the intensity of scattering is given by the relation

[2] B. E. Warren, Phys. Rev. **45**, 657 (1934).
[3] F. C. Blake, Rev. Mod. Phys. **5**, 180 (1933).
[4] B. E. Warren and N. Gingrich, Phys. Rev. **46**, 368 (1934).
* If there are two kinds of carbon atom then $\rho(r)$ is the average of the two density functions.

$$I(s) = N\psi(s)\left\{1 + \int_0^\infty 4\pi r^2 \rho(r)\,(\sin sr)/sr\,dr\right\}, \quad (1)$$

where

$$\psi(s) = I_0 e^4 f^2 ((1+\cos^2 2\theta)/2)/m^2 c^4 R^2,$$

$s = 4\pi \sin\theta/\lambda$ and N is the effective number of atoms in the sample.

Let

$$i(s) = I(s)/N\psi(s) - 1,$$

$$si(s) = 4\pi \int_0^\infty r\rho(r) \sin sr\,dr. \quad (2)$$

By the Fourier integral theorem this can be written

$$r\rho(r) = (1/2\pi^2)\int_0^\infty si(s) \sin sr\,ds. \quad (3)$$

The integration over the scattered intensity $I(s)$ is from zero to large angles, and hence includes the diffraction maximum at zero angle (000 order) which is not experimentally observable. Replace $I(s)$ by $I'(s) + I(s)$ where $I'(s)$ is the intensity distribution in the 000 order beam, and $I(s)$ is the observable intensity curve.

That part of the integral in Eq. (3) which involves $I'(s)$ is readily evaluated and takes the same value for either an amorphous or crystalline material. Eq. (3) then takes the final form

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^{\infty} si(s) \sin sr\, ds, \quad (4)$$

where ρ_0 is the average density of the sample in atoms per cc. The curve $si(s)$ can be obtained directly from the experimental intensity curve and the integration involved in Eq. (4) then readily carried out with a harmonic analyzer. By a purely mechanical, straightforward method, one obtains the distribution curve $4\pi r^2 \rho(r)$ directly from the experimental intensity curve.

Application of carbon black

The experimental intensity curve is given by Fig. 1a, the intensity being expressed in arbitrary units. As seen from Eq. (1) at large angles of scattering $I(s)$ approaches $N\psi(s)$ and hence at sufficiently large values of $\sin \theta/\lambda$ the experimental curve is given by the modified and *independent* unmodified scattering of N atoms.

Independent unmodified $I = N\psi(s)$

Modified[5] $I = NI_0 \dfrac{e^4}{m^2 c^4 R^2} \left(\dfrac{1 + \cos^2 2\theta}{2} \right) \{Z - \Sigma f_n^2\}.$

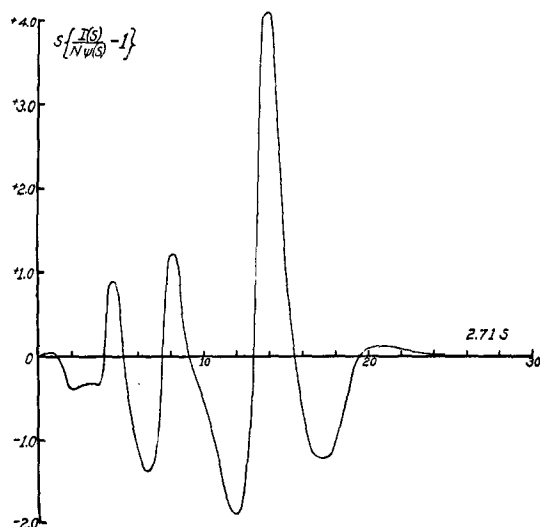Assuming that the scattering can be taken as

Fig. 2. Curve $si(s)$ plotted against s.
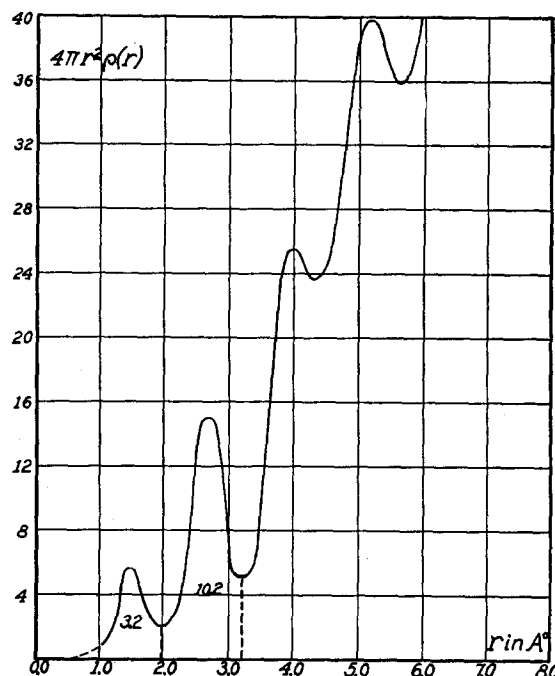
[5] E. O. Wollan, Rev. Mod. Phys. **4**, 233 (1932).

Fig. 3. Distribution of surrounding atoms in carbon black.

independent at $\sin \theta/\lambda = 0.6$, the fractional parts of unmodified and modified scattering are calculated. Since $I = I_{unmod.} + I_{mod.}$ this determines the ordinates at $\sin \theta/\lambda = 0.6$ for both the modified and independent unmodified curves. Both of these curves are readily calculated as a function of the angle, from the tables of scattering factors[6] and, the scale of ordinates having been fixed at one point, the two curves are then plotted on the same scale as $I(s)$. The unmodified part of the experimental scattering curve is then obtained by subtracting 1b from 1a. The difference divided by 1c gives the quotient $I(s)_{coh}/N\psi(s)$ from which the curve $si(s)$ is constructed. Although the assumption of independent scattering at large angle is only an approximation, it is nevertheless a sufficiently good one, and affords a very simple method of putting the $si(s)$ curve upon a quantitative basis.

The curve $si(s)$ obtained in this way is plotted against s (Fig. 2) and the integration involved in Eq. (4) carried out on a Coradi harmonic analyzer. The coefficients which the analyzer delivers for the different harmonics give directly the values of the integral for various values of r.

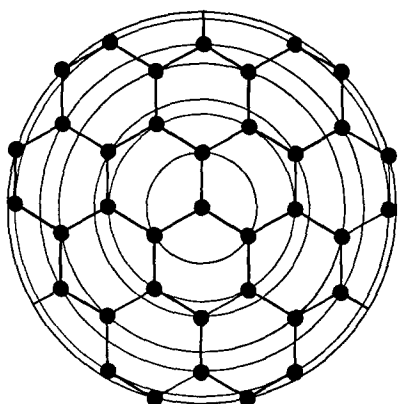[6] James and Brindley, Phil. Mag. **12**, 81 (1931).

Fig. 4. Atomic arrangement in a single layer of the graphite structure.

Table I. *Number of neighbors and distances in a single graphite layer.*

No.	Distance	Aver. Distance
3	1.42A	
6	2.46 ⎫	
3	2.84 ⎭	2.6A
6	3.75 ⎫	
6	4.25 ⎭	4.0
6	4.92 ⎫	
6	5.11 ⎭	5.0

The scale of abscissae used in Fig. 2 corresponds to 0.425A per harmonic and the integration was carried out for the first 15 harmonics, thus giving points on the r scale from 0 to 6.4A. By then altering the scale of abscissae in Fig. 2, intermediate points were obtained.

The density curve so obtained is shown in Fig. 3. From the curve one gets directly the concentration of atoms at any distance from a given atom and, furthermore, since the work has been carried through on a quantitative basis, the areas under the peaks give directly the number of atoms in that range of distances.

At a distance of about 1.5A there is a peak containing 3.2 atoms, at 2.7A a peak containing 10.2 atoms and further concentrations at 4.05A and 5.15A. The curve indicates that the atomic arrangement in carbon black is definitely not diamond-like, since in the diamond structure there are 4 neighbors at 1.54A, 12 at 2.52A and 12 at 2.95A. Allowing for slight errors in the number of atoms and positions of the peaks due

to overlapping, the distribution of Fig. 3 is in very close agreement with that of a *single* graphite layer.

The atomic arrangement in a single layer of the graphite structure is represented in Fig. 4 and the number of neighbors and their distances are tabulated in Table I.

The correspondence with the distribution of Fig. 3 is sufficiently close to justify the conclusion that *single* graphite layers exist in carbon black. Beginning at about 3.6A, there is a marked continuous distribution which is due to the atoms in neighboring layers. If these neighboring layers have a definite position and orientation with respect to the first layer, the configuration is that of graphite; if they do not, then carbon black is a mesomorphic form of carbon (regular arrangement in two dimensions only). It is very difficult to decide between these two possibilities.

Fig. 5 (a) shows the atom distribution for graphite crystals. Fig. 5 (b) gives the distribution for a material consisting of single graphite layers,
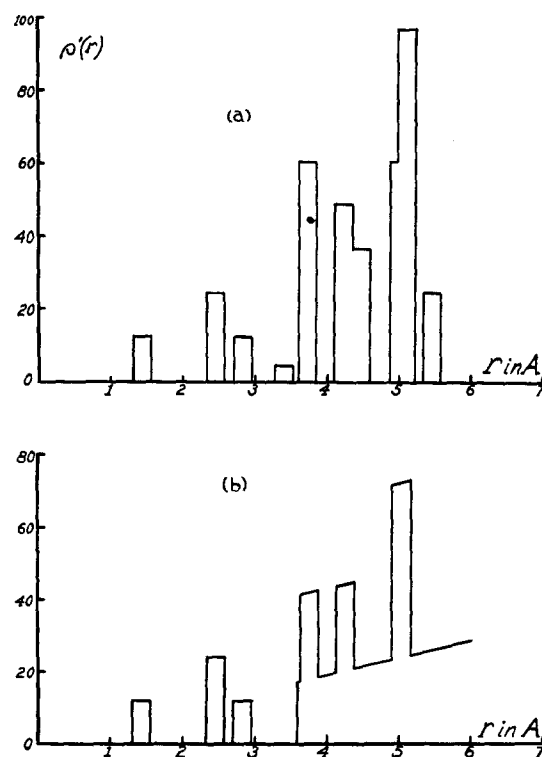

Fig. 5. (a) Atom distribution in a graphite crystal. (b) Atom distribution in a mesomorphic form of carbon, consisting of single graphite layers stacked roughly parallel to one another.

roughly parallel to one another and having an average separation of 3.6A. For a non-crystalline stacking of the single graphite layers, it would, of course, be expected that the layer separation would be slightly larger than the distance 3.4A, characteristic of graphite.

The two distributions are not sufficiently different to allow either one to be definitely excluded. In fact, from the experimental distribution curve one can only conclude that carbon black consists of either extremely small graphite crystals or single graphite layers roughly parallel to one another or a heterogeneous mixture of these two. The fact that the experimental scattering curve *could* be satisfactorily interpreted on a basis of single graphite layers roughly parallel to one another is extremely interesting and should be a warning against drawing too hasty conclusions from a diffraction pattern which shows only two or three diffuse peaks. Although the exact numerical values involved in the distribution curve of Fig. 3 should not be relied upon too closely, it is, however, worth noting that the area under the curve is in better agreement with a structure of single graphite layers roughly 3.8A apart than with a structure of small graphite crystals. On the other hand, the small angle scattering, discussed in the next section, indicates that at least a fraction of the material is in the form of small graphite crystals. It is probable that the average sample of carbon black is a heterogeneous mixture of particles ranging from single graphite layers up to graphite crystals several layers thick.

Small angle scattering

Referring to Fig. 1a it will be noticed that the diffraction pattern of carbon black shows one feature which is very unusual for homogeneous solids and liquids. Instead of the intensity falling to a small value with decreasing angle, it rises to a value which is actually greater than that of the strongest peak. This fact has been noticed by other investigators[1c, h] and several rather complex explanations have been put forward.

The effect appears to be due solely to the fact that the material consists of extremely fine grains which, because of their very flat non-uniform shape, pack together very loosely in the sample. About any atom there is accordingly a region of high density extending out to a distance which is of the order of magnitude of the grain size and beyond this an average density which is necessarily lower due to the loose packing of the grains. If this type of distribution be inserted in Eq. (1), we find that the intensity at small angle may have very appreciable values depending upon the amount of excess density. If we assume that a fraction of the material is in the form of small graphite crystals several layers thick, the difference between the density of graphite and carbon black is enough easily to account for the observed intensity at small angle. The decrease of the small angle scattering with increasing angle depends upon the dimensions of the high density region and is thus a rough measure of grain size.

Conclusions

Carbon black is not a truly amorphous form of carbon. The existence of single graphite layers is very definite and therefore the material is at least mesomorphic. The diffraction data indicate a heterogeneous mixture containing particles which range from single graphite layers up to graphite crystals several layers thick. The size of the grains will vary widely from one sample to another, depending upon the method of formation, and it is probably true that carbon black comprises a continuous series extending from the mesomorphic to the crystalline state.