

X-RAY STUDY OF THE GRAPHITIZATION OF CARBON BLACK*

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A typical carbon black consists of parallel layer groups which give rise to 00ℓ crystalline reflections and two-dimensional reflections hk . Approximate parallel layer group dimensions L_a and L_c can be obtained from the peak breadths. The first effect of heat treatment is to increase the layer group dimensions. At higher temperatures, pairs of nearest neighbor layers take on the graphite relation. In the beginning, the ordering of nearest neighbor pairs is completely independent of all neighboring layers, and both ABC and ABA sequences are produced. The ordering produces modulations in the 2-dimensional hk reflections, and from these modulations we obtain P_1 , the probability of nearest neighbor ordering. For partial graphitization there are two different nearest layer spacings, and allowance must be made for this in measuring the L_c dimension. Correction must be made for the modulations in the hk reflections in computing the L_a dimensions. The principles are illustrated by a set of measurements on Fine Thermal black heat treated to produce various degrees of imperfections.

I. INTRODUCTION

The structure of carbon black can be described in terms of the graphite structure shown by Fig. 1. Graphite has a layer structure with a layer spacing of 3.35\AA . Each carbon in a layer is bonded to 3 neighbors at 1.42\AA , forming a two dimensional hexagonal net. In the graphite structure, half of the atoms in a layer are directly over atoms in the previous layer, and the other half are over the centers of the hexagons. The second layer is directly over the zero layer, so that the c axis is twice the layer spacing.

The average carbon black without additional heat treatment gives an x-ray pattern with only 3 diffuse peaks, from which it is not possible to deduce a unique structure. With heat treatment the pattern sharpens sufficiently to allow a definite structure determination, and from the structure of the heat treated black it is possible to surmise the structure of the original black. The x-ray studies indicate that carbon black is made up of graphite layers roughly parallel to one another but

with random orientation about the layer normal, and a layer spacing somewhat larger than that of graphite. The average carbon black without additional heat treatment consists of parallel layer groups in which there are 4 or 5 such roughly parallel graphite layers. The dimensions of the parallel layer groups normal to the layers and parallel to the layers are called L_c and L_a . Values of the order $L_c = 12\text{\AA}$ and $L_a = 20\text{\AA}$ are common for untreated blacks. Presumably the parallel layer groups result from the packing together of the disk-shaped graphite layers, the larger the disk diameter the larger the number of layers in the group.

Figure 2a shows the x-ray pattern of a carbon black with the usual three diffuse rings. Figure 2b is a pattern of the same black heated 2 hours at 2000°C . The pattern consists of the (00ℓ) crystalline reflections (002) and (004) , and the 2-dimensional (hk) reflections (10) and (11) . Figure 3 shows the microphotometer record of the 2-dimensional reflection (10) . It rises sharply to a peak and then falls off slowly on the high angle side, with the crystalline reflection (004) superimposed on the high

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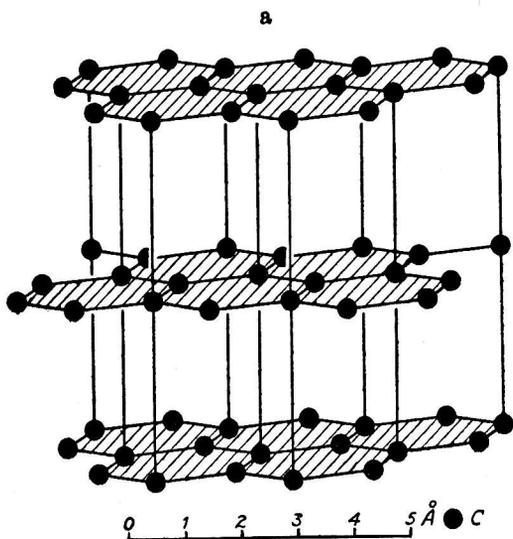


FIG. 1. The structure of graphite

angle tail. This type of 2-dimensional lattice reflection would be produced by individual graphite layers taking independently all orientations in space. Since the $(00l)$ reflections prove that there are several graphite layers roughly parallel, it is the observance of the 2-dimensional reflections which proves that in the parallel layer groups the layers have random orientations about their normals. The layer diameter L_a is obtained directly from the half-maximum breadth of the 2-dimensional reflections by the 2-dimensional particle size equation^{1, 2}.

$$L_a = \frac{1.84 \lambda}{B \cos \theta} \quad (1)$$

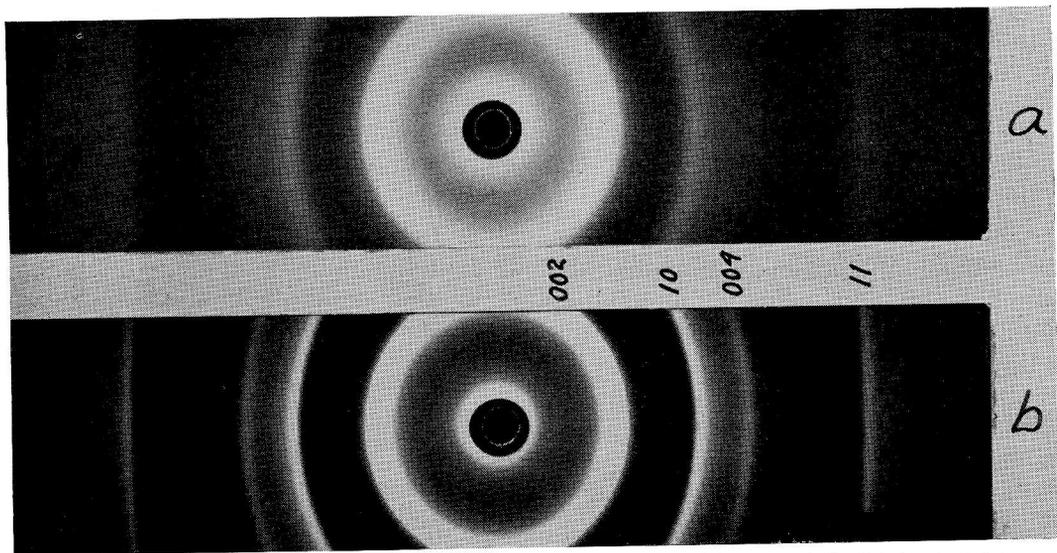


FIG. 2. X-ray diffraction patterns of Spheron Grade 6 black, (a) untreated, (b) heated 2 hours at 2000°C. Radiation $\text{CuK}\alpha$.

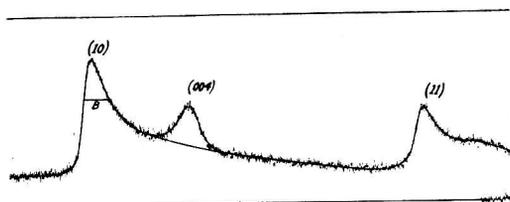


FIG. 3. Microphotometer record showing the 2 dimensional reflection (10), Spheron Grade 6 black heated 2 hours at 2800°C.

II. GROWTH OF PARALLEL LAYER GROUPS BY HEAT TREATMENT

The first effect of heat treatment on a carbon black is to cause an increase in the size of the parallel layer groups. Figure 4 shows the sharpening of the pattern of a

¹ B. E. Warren, *Phys. Rev.* **59**, 693 (1941).

² J. Biscoe and B. E. Warren, *Jour. Appl. Phys.* **13**, 364 (1942).

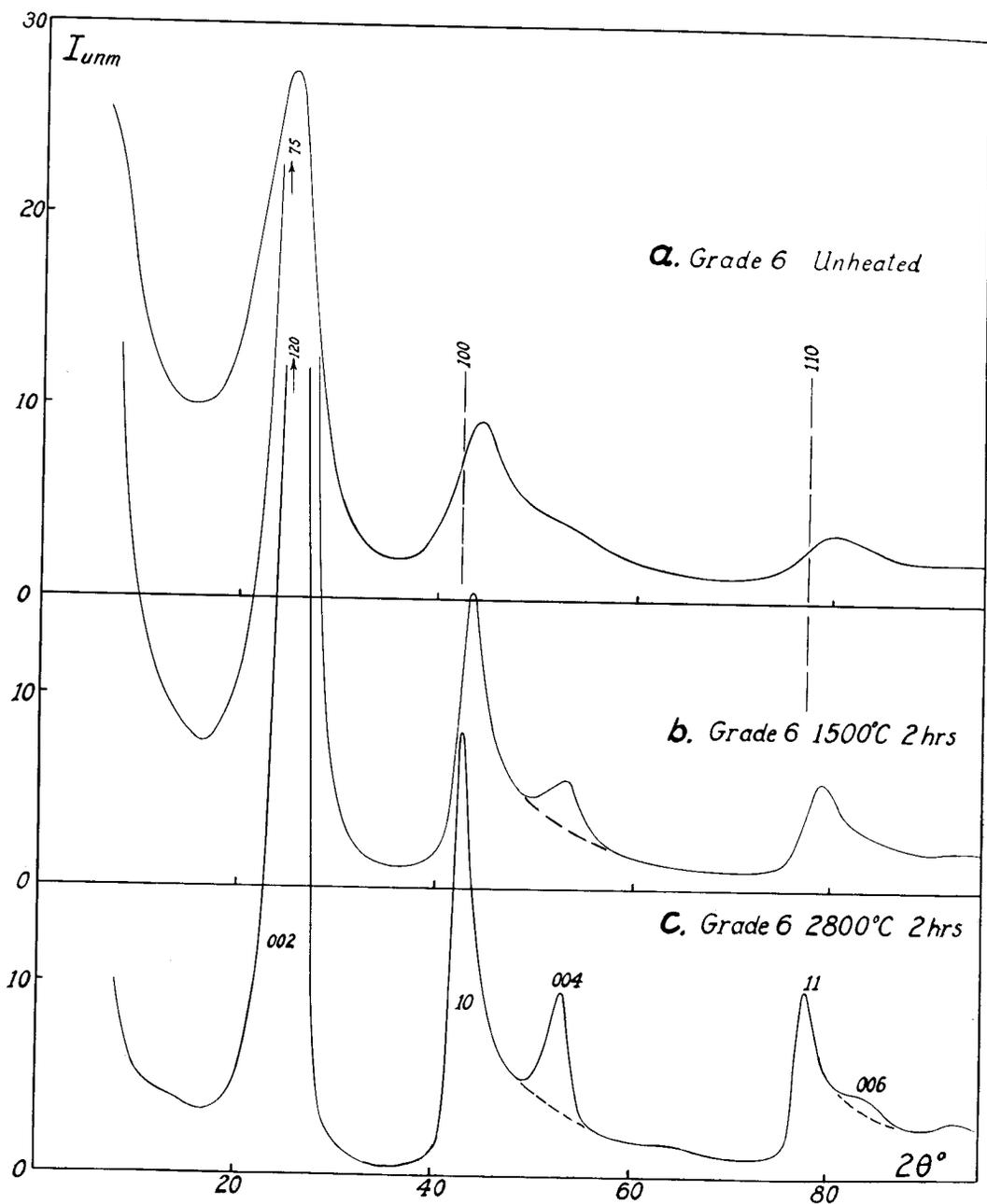


FIG. 4. Sharpening of intensity curves for Spheron Grade 6 black; (a) untreated, (b) heated 2 hours at 1500°C, (c) heated 2 hours at 2800°C.

Spheron Grade 6 black by heat treatment. The (hk) 2-dimensional reflections sharpen considerably, but retain the characteristic shape of a 2-dimensional reflection, in-

dicating that the layer diameters L_a increase, but the orientations of the layers about their normal remains random. The $(00l)$ reflections also sharpen indicating an

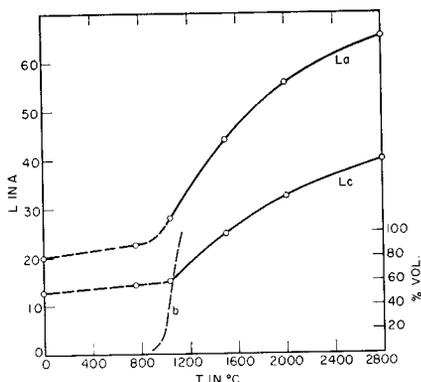


FIG. 5. (a) The dimensions L_a and L_c of the parallel layer groups in Spheron Grade 6 black heated for 2 hours at various temperatures, (b) per cent by volume of H_2 in gas evolved.

increase in the average number of layers in a parallel layer group, and corresponding increase in the dimension L_c .

The increase in the L_a and L_c dimensions on heat treatment is shown by Fig. 5 for the Spheron Grade 6 blacks. Appreciable growth starts at around 1000°C , which is also the temperature at which there is a rapid increase in the rate at which H_2 is driven off. It seems very reasonable that growth should not start until the hydrogen bound to the edges of the layers is removed. The x-ray measurements do not suffice to distinguish between layer growth by individual atoms moving from one layer and joining another, or the moving of a whole layer to join another layer. The fact that there is an increase in the average number of layers in a parallel layer group suggests that there is a motion of whole layers.

In the Spheron 6 blacks the layers remain random in orientation about their normals, even up to 2800°C , where the layer diameter has reached a value of the order $L_a = 65\text{\AA}$. In some blacks, even at temperatures well below 2800°C , the layers are no longer completely random about their normals, but pairs of nearest neighbor layers start to take on the graphite relation. This process seems to start when the layer diameters reach the order of $L_a = 100\text{\AA}$

as has been pointed out by Franklin³. The attraction between two parallel graphite layers should increase, and the periodic structure of the layer should become important as the layer diameter increases. Presumably it is only for values greater than $L_a = 100\text{\AA}$ that there is an appreciable decrease in energy by the two parallel layers rotating to take on the definite graphite relation.

III. THE BEGINNING OF GRAPHITIZATION

When neighboring layers in a parallel layer group start to assume the graphite relation, modulations appear in the (hk) 2-dimensional reflections⁴. Figure 6 shows the appearance of modulations in the (10) 2-dimensional reflections from a Fine Thermal black which reaches $L_a = 100\text{\AA}$ at about 2000°C . The modulations which are seen are the beginning of the splitting up into (100) and (101) . When two neighboring layers order, there is a decrease in the layer spacing and the (004) reflection moves toward larger angle. Figure 7 shows the appearance of modulations in the (11) reflection on heat treating the same black. The modulations here are very pronounced and represent the beginning of the splitting of (11) into (110) and (112) .

With the beginning of modulations, the problem of measuring L_a and L_c becomes much more difficult. The modulations increase the width of (10) and decrease the width of (11) , so that unless corrections are made for the modulations, quite inconsistent values of L_a are obtained. Since ordering of nearest neighbor layers reduces the layer spacing, a partially ordered sample contains a range of average spacings, and the breadth of the (00ℓ) reflections is due to both the L_c dimension and this spacing variation. Unless correction is made for

³ R. E. Franklin, *Acta Cryst.* **3**, 107 (1950); *Acta Cryst.* **4**, 253 (1951); *Proc. Roy. Soc.* **A209**, 196 (1951).

⁴ C. R. Houska and B. E. Warren, *Jour. Appl. Phys.* **25**, 1503 (1954).

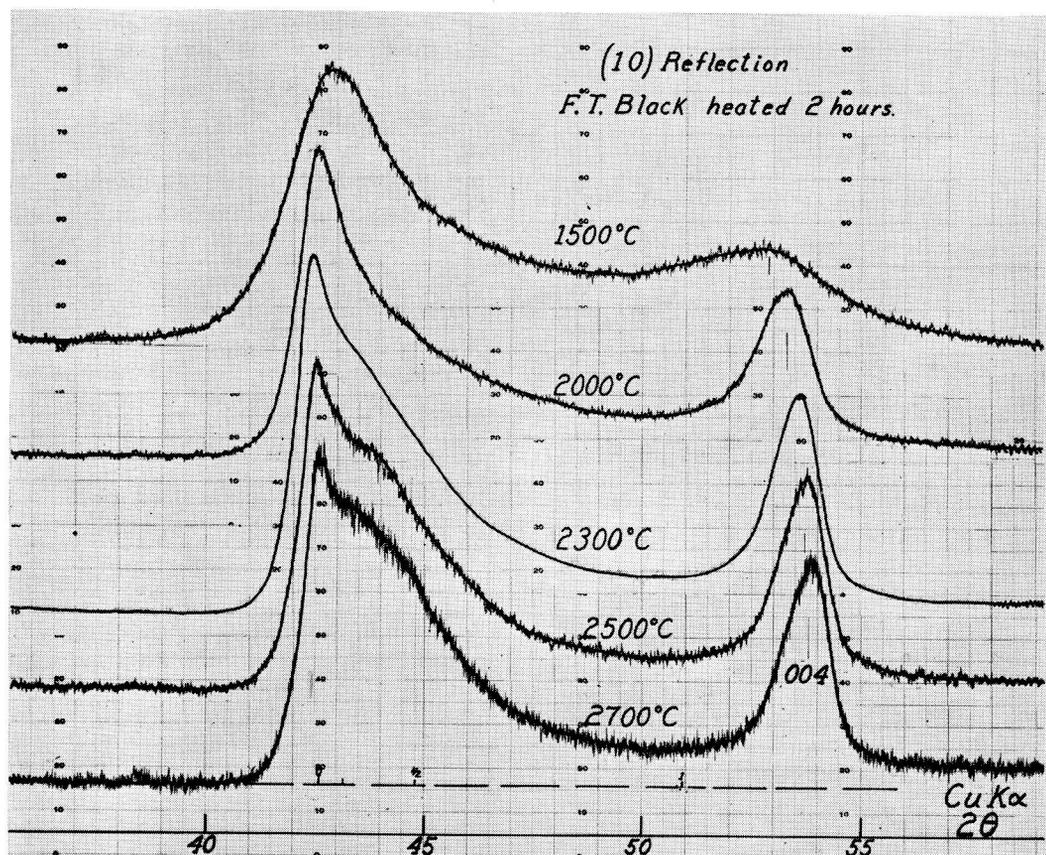


Fig. 6. Development of modulations in the (10) reflection of a fine thermal (FT) black heated 2 hours at various temperatures.

the spacing variation, (004) gives a smaller L_c value than (002).

As long as the graphite layers in a parallel layer group have random orientations about the layer normals, the reciprocal lattice consists of sharp (00 l) points and uniform (hk) rods. Ordering shows up by a periodic density variation in the (hk) rods. It is these periodic density variations which produce the modulations in the (hk) reflections. For an (hk) reflection which shows modulation, the ordinate of the diffractometer trace, except in the vicinity of the peak, can be approximated by⁴

$$P_{2\theta}'(hk) = \frac{kjF^2(1 + \cos^2 2\theta)}{4 \sin \theta (\sin^2 \theta - \sin^2 \theta_0)^{\frac{1}{2}}} \cdot \sum_{n=-\infty}^{+\infty} A_n(hk) \cos 2\pi n h_3 \quad (2)$$

where K is a constant

j is the 2-dimensional multiplicity
 F is the 2-dimensional structure factor, $F^2 = 4f^2 \cos^2 [\pi(2h + k)/3]$.
 θ_0 is the Bragg angle corresponding to the reflection ($hk0$).

h_3 is the variable of the Fourier series; it is proportional to a distance along the (hk) rod, and is given by

$$h_3 = (\sin^2 \theta - \sin^2 \theta_0)^{\frac{1}{2}} 2a_3 / \Lambda \quad (3)$$

a_3 is the spacing of the graphite layers.

$A_n(hk)$ is the coefficient of the Fourier series, $A_n(hk) = \langle \exp [2\pi i(X_n h + Y_n k)] \rangle$ where $X_n a_1$ and $Y_n a_2$ are the displacements of a layer with respect to its n th neighboring layer. For pairs of ordered layers, X_n and Y_n have definite values, while for dis-

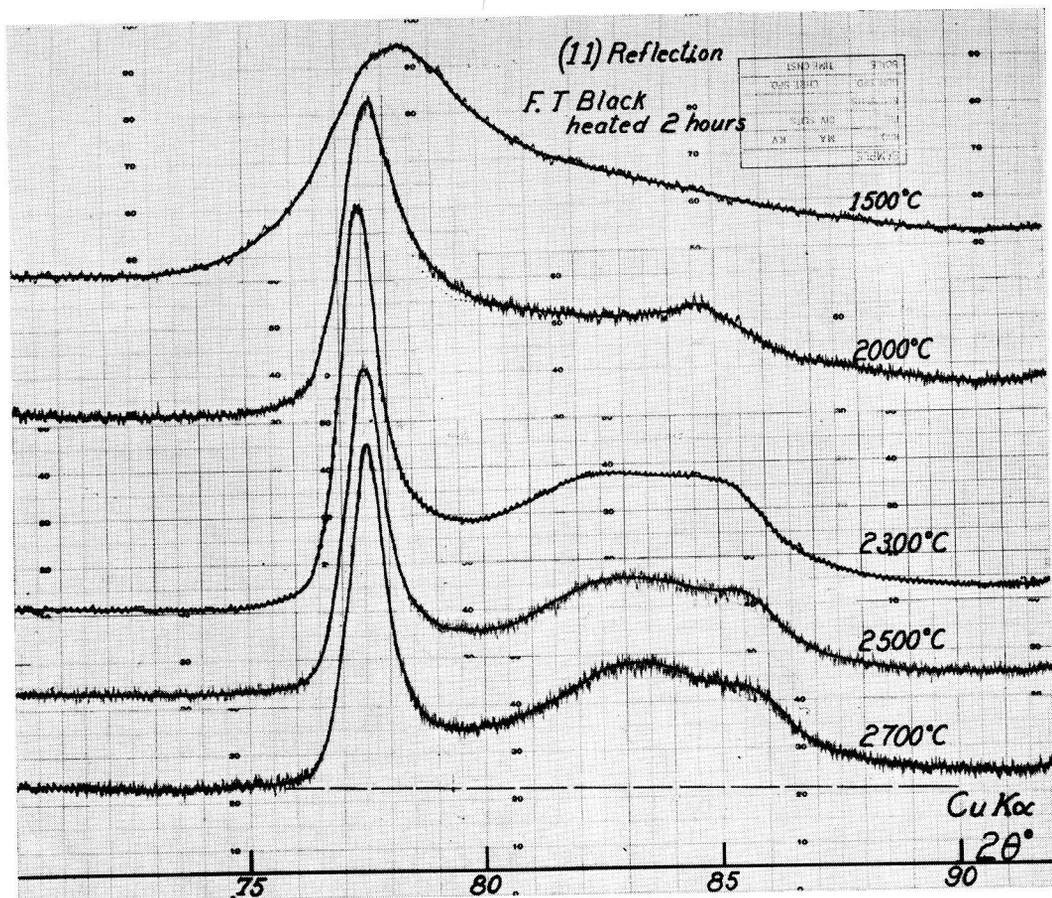


FIG. 7. Development of modulations in the (11) reflection of a fine thermal (FT) black heated 2 hours at various temperatures.

ordered pairs $\langle \exp [2\pi i(X_n h + Y_n k)] \rangle$ is zero.

By dividing the experimentally observed quantity $P_{2\theta}'(hk)$ by the terms preceding the summation in Eq. (2), and normalizing by the condition that $A_0(hk) = 1$, we obtain the experimental modulating factor $\sum_n A_n(hk) \cos 2\pi n h_3$ in absolute units. This expression is a Fourier series and it is periodic in h_3 . From any reliable half period in the curve, the coefficients $A_n(hk)$ can be determined in the usual way by use of the Lipson and Beevers strips.

IV. EXPERIMENTAL DIFFICULTIES

The crystalline reflections (002) and (004), and the 2-dimensional reflections (10) and

(11) contain the data required for following the graphitization of carbon black. Most of the early work in this field was done with crystal monochromated radiation, evacuated cameras, and film recording. Today quantitative work is better done with recording Geiger counter diffractometers. Using doubly bent LiF monochromators, CuK α radiation, and dispensing with the usual Soller slits, there is enough intensity for direct recording of carbon black patterns. For most work however it is simpler and adequate to use filtered radiation with the commercial diffractometers. In some cases where special studies of diffuse background intensities must be made, the use of balanced

filters gives a good enough approximation to monochromatic radiation.

For carbon black there is a serious source of trouble in using recording diffractometers with the usual flat faced powder briquet sample. The geometry of the diffractometer assumes that diffraction takes place only in the surface of the sample, and most materials have sufficiently high absorption coefficients for this to be a good approximation. However for carbon black the absorption is so small that the beam penetrates well into the sample, diffraction takes place in the interior of the sample, and this produces an asymmetric broadening and peak shift toward small angle on the recording. The effect can be eliminated by using a sample so thin that interior diffraction can be neglected, but for carbon black the corresponding loss in intensity can seldom be tolerated. Another method is to use the standard thick sample, and then correct the shape of the peak for the small absorption effect by using the published correction methods⁵. The correction by means of the derivative of the measured curve using Eq. 5 of Reference 5 is made simple by working with a sample at least 3 mm thick so that only the first two terms of the equation are needed. The correction can be made smaller by using $\text{CrK}\alpha$ radiation rather than the usual $\text{CuK}\alpha$. The disadvantage to doing this comes from the fact that the ratio of the effective $\text{K}\alpha$ intensity to the general background is much lower with Cr radiation. For material with small L_a and L_c , where the peaks are broad and the corrections of only small importance, it is best to use $\text{CuK}\alpha$. For materials having sharp $(00l)$ and sharp modulations in the (hk) reflections, the small absorption correction is very important, and it is worthwhile using $\text{CrK}\alpha$.

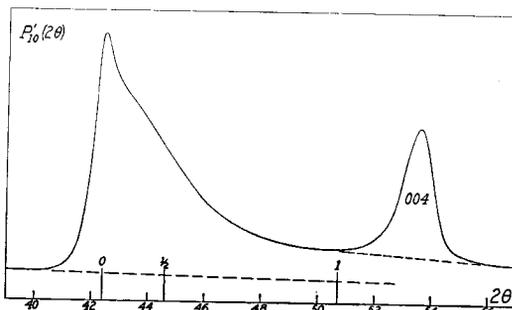


FIG. 8. The (10) reflection from (FT) black heated 2 hours at 2300°C, $\text{CuK}\alpha$ radiation.

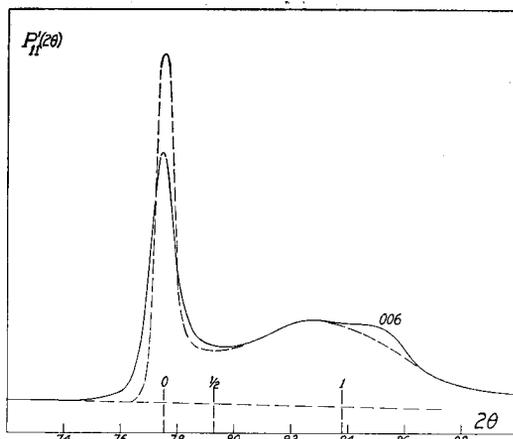


FIG. 9. The (11) reflection from (FT) black heated 2 hours at 2300°C, $\text{CuK}\alpha$ radiation. Dashed peak, corrected for instrumental broadening.

V. EVALUATION OF PATTERNS WHEN MODULATIONS ARE PRESENT

The evaluation of a pattern showing modulations will be illustrated by a Fine Thermal black⁶ heated 2 hours at 2300°C. This black has an electron microscope average particle diameter of 1600Å, and the surface characteristics of similarly heat-treated blacks have been reported^{7, 8}. Figure 8 shows the diffractometer trace for the (10) reflection using $\text{CuK}\alpha$. The crystalline

⁶ W. Schaeffer, W. R. Smith and M. Polley, *Ind. Eng. Chem.* **45**, 1721 (1953).

⁷ M. Polley, W. Schaeffer and W. R. Smith, *J. Phys. Chem.* **57**, 469 (1953).

⁸ R. A. Beebe and D. M. Young, *J. Phys. Chem.* **58**, 93 (1954).

⁵ D. T. Keating and B. E. Warren, *Rev. Scient. Inst.* **23**, 519 (1952).

reflection (004) is eliminated by drawing a smooth curve under it. The background line for the (10) reflection is well defined on the small angle end. To fix the height of the background line on the right hand end we lay off the values of the variable $h_3 = 0, 0.5, 1.0$ and 1.5 using Eq. 3. From Eq. (2), the ordinates of the curve divided by the terms preceding the summation should give the Fourier series $\sum_n A_n(hk) \cos 2\pi n h_3$, and this is periodic in h_3 . The corrected curve should have equal heights at $h_3 = 0.5$ and $h_3 = 1.5$. Since the background height can be guessed at $h_3 = 0.5$, this condition fixes it at $h_3 = 1.5$.

Figure 9 shows the diffractometer trace for the (11) reflection. The (006) reflection is eliminated by drawing a smooth curve, and the height of the background fixed in the same way as for the (10) reflection. Using $\text{CuK}\alpha$, the broadening by the small absorption effect is particularly bad for the sharp peak at the small angle end of the (11) reflection. The effect is readily corrected by use of the derivative of the curve⁵. The next most important correction is that for the extraneous broadening due to the unresolved $\alpha_1\alpha_2$ doublet. This is readily corrected by the methods of DuMond⁹ and Rachinger¹⁰, or by a Stokes¹¹ type Fourier method. The dotted line of Fig. 9 illustrates the importance of the correction. The relative magnitude of both of these corrections would be decreased by using $\text{CrK}\alpha$.

Excluding the part near the peak, the corrected (10) and (11) curves are divided by the terms preceding the summation in Eq. 2, and plotted against the variable h_3 defined by Eq. 3. Since the quantity obtained is a periodic Fourier series, a half period suffices. The function is normalized by the condition that $A_0(hk) = 1$. From the

normalized curves, the Fourier coefficients $A_n(hk)$ are readily obtained by use of the Lipson and Beever's strips. The values obtained from the (10), (11) and (21) reflections are given in Table I. If nearest neighbor pairs order independently there should be a relation between the coefficients⁴ $A_n(hk) = [A_1(hk)]^{|n|}$. The values in Table I obey this relation very closely, indicating that in the early stages of graphitization nearest neighbor pairs order independent of neighboring layers.

The Fourier coefficients can be expressed in terms of probabilities for the displacement of an n th neighbor layer

$$\begin{aligned} P_n^0 & \text{ probability of zero displacement} \\ P_n^+ & \text{ probability of displacement} \\ & X_n = \frac{2}{3}, \quad Y_n = \frac{1}{3} \\ P_n^- & \text{ probability of displacement} \\ & X_n = -\frac{2}{3}, \quad Y_n = -\frac{1}{3} \end{aligned}$$

Since P_n^+ and P_n^- are equally probable

$$A_n(hk) = P_n^0 + (P_n^+ + P_n^-) \cos 2\pi \left(\frac{2}{3}h + \frac{1}{3}k \right) \quad (4)$$

Using the condition that $P_1^0 = 0$ (nearest neighbors cannot be directly above one another), the coefficients in Table I can be used to compute the probabilities of Table II. P_1 is the probability of nearest neighbor layers being ordered, P_2^0 is the probability

TABLE I
Coefficients $A_n(hk)$ for FT Black Heated 2 Hours at 2300°C

n	$A_n(10)$	$A_n(11)$	$A_n(21)$
0	1.00	1.00	1.00
1	-0.13	0.25	-0.12
2	0.02	0.06	0.02

TABLE II
Probabilities of First and Second Neighbor Ordering in (FT) Black Heated 2 Hours at 2300°C

$P_1 = (P_1^+ + P_1^-) = 0.25$
$P_2^0 = 0.033$
$(P_2^+ + P_2^-) = 0.027$

⁹ J. W. M. DuMond, Rev. Mod. Phys. **5**, 1 (1933).

¹⁰ W. A. Rachinger, J. Scient. Inst. **25**, 254 (1948).

¹¹ A. R. Stokes, Proc. Phys. Soc. **61**, 382 (1948).

of second neighbor layers being in the ABA sequence, and $(P_2^+ + P_2^-)$ is the probability of second neighbor layers being in the ABC sequence. Within the experimental error we can say that one quarter of the nearest neighbor pairs are ordered, one sixteenth of the second neighbor pairs are ordered, and for the latter there is about equal probability of following ABA and ABC sequences. Since there is about equal probability of ABA and ABC ordering in the early stages of graphitization, stacking faults are probably to be expected in graphite obtained by graphitizing a black.

Having determined the modulating factor $\sum_n A_n(hk) \cos 2\pi n h_3$, the experimental curves for (10) and (11) can be demodulated by dividing by the modulation factor. Using Eq. (1), we can then obtain L_a values from the half-maximum breadths of the demodulated curves. It is also possible to obtain approximate values of P_1 and L_a directly from the (hk) curves by means of a logarithmic plot⁴. These values are in general less accurate than those obtained by the process of demodulation.

When modulations appear in the (hk) reflections there are two slightly different layer spacings, and the (00ℓ) reflections are broadened by both particle size and distortion. The distortion broadening must be corrected, otherwise inconsistent values of L_c will be obtained from (002) and (004). To

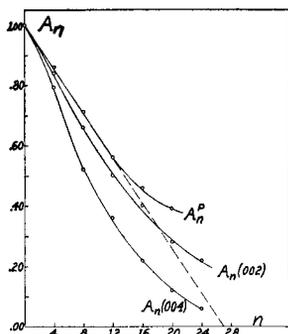


FIG. 10. The Fourier coefficients $A_n(\ell)$ for (002) and (004) and the particle size coefficient A_n^P for (FT) black heated 2 hours at 2300°C.

TABLE III
Numerical Values for an (FT) Black Heated 2 Hours at Various Temperatures

T	$\langle l_c \rangle$	P_1	L_a
°C	A		A
2000	59	0.03	97
2300	72	0.25	129
2500	78	0.33	136
2700	88	0.35	132

do this, the reflections are corrected for instrumental broadening, the corrected shapes represented by a Fourier series, and the Fourier coefficients determined. Figure 10 shows the Fourier coefficients obtained from the (002) and (004) reflections. If there were no distortion broadening (variation in layer spacing), the (002) and (004) curves would coincide. In terms of $\ell = 1$ for (002) and $\ell = 2$ for (004), we extrapolate to $\ell = 0$ by plotting $\ln A_n(\ell)$ vs. ℓ^2 for each value of n . The coefficients obtained, A_n^P represent broadening due to particle size only; they are also shown on Fig. 10. From the initial slope of the A_n^P curve, a mean parallel layer group thickness $\langle L_c \rangle$ is obtained. The coefficients A_n^P could also be used to obtain the usual half-maximum intensity breadth of the (00ℓ) reflection due to particle size only. From such a breadth we obtain another kind of average $\langle L_c^2 \rangle / \langle L_c \rangle$.

Table III gives numerical values for the same (FT) black heated 2 hours at various temperatures. L_c is the thickness obtained from the initial slope of the A_n^P curve. P_1 and L_a were obtained from the (10) reflection by use of the logarithmic chart. P_1 is the probability of nearest neighbor pairs of layers ordering to take on the graphite relation. It is an ideal quantity to define as the "degree of graphitization."

VI. DISCUSSION

X-ray studies of heat treated carbon blacks are capable of giving a fairly detailed picture of the structure of the original carbon black, and of the process of graphiti-

zation. The original carbon black contains small graphite layers with diameters of the order $L_a = 20\text{\AA}$. Due presumably to the disk shape of the layer, several of these layers tend to pack roughly parallel forming parallel layer groups. In the original black there are some 3 or 4 or 5 layers in a parallel layer group, corresponding to a layer group thickness of the order $L_c = 12\text{\AA}$. The graphite layers in a parallel layer group are roughly parallel but random in orientation about the layer normal. At this stage, the layers are held together by very weak van der Waals forces, and the layer spacing is larger than that of crystalline graphite. The layer is too small to make its periodic structure be felt, and there is no tendency for a layer to take a definite orientation with respect to neighboring layers.

With heat treatment the layers start to grow in diameter, either by migration of individual atoms from one layer to a growing layer, or by joining together of layers. At the same time the number of layers in a parallel layer group increases, suggesting that displacements of the layers are taking place. In the first stage of growth of the parallel layer groups, the layers remain random in orientation about the layer normal.

When the layer diameter reaches a value of the order $L_a = 100\text{\AA}$, pairs of nearest neighbor layers show a tendency to take on the graphite relation. With increasing layer diameter the attraction between the layers

increases, the separation decreases, and the potential minima corresponding to a graphite relation begin to be felt. Different blacks show different L_a growth with temperature. Ordering seems to start at the temperature for which the L_a value reaches the order of 100\AA . In the beginning, pairs of nearest neighbor layers order independently, rather than whole regions taking on the graphite structure. This independence in ordering produces ABC as well as ABA sequences. For an ordered pair the layer spacing decreases to approximately the graphite value^{3, 12} 3.35\AA . Ordering of the layers is the beginning of graphitization, and this effect can be recognized by the appearance of modulations in the (hk) reflections. From the modulations it is possible to evaluate the parameter P_1 , the probability of nearest neighbor pairs ordering to the graphite relation. It is suggested that P_1 is a suitable quantity to define as the "degree of graphitization."

Much of the work described here parallels the studies of carbon made by Miss R. E. Franklin and her publications³ should be read to get as broad a picture as possible. The results which have been reported here have been taken from the work of J. Biscoe, C. R. Houska, and Mrs. M. Dano.

We are indebted to Dr. W. R. Smith of Godfrey L. Cabot, Inc. for his very generous help and advice throughout the course of these studies.

¹² G. E. Bacon, *Acta Cryst.* **4**, 558 (1951).