TABLE I. Averages of measurements from oscilloscope records.

Applied potential 200 volts
$C=2\times 10^{-9}$ f
Electrode separation 1 mm

(1) Inductance	(2) Arc voltage Initial	(3) Mean	(4) Main	(5) Final voltage	(6) Circuit res.	(7) Max. current	(8) Max. current density
(10^{-6} h)					(ohms)	(amp.)	(amp./cm²)
3.3		33.5		−98	6	4.0	4×10^{6}
48.3	76		37	−109	12	1.0	1×10^{6}

the initial rate of current increase is only slightly greater than the above value of 10^6 amp./sec.

In these arcs it is of course necessary that there be enough positive ions produced to prevent space charge limitation of the current density. Langmuir[12] has shown that ions produced at the anode can increase the maximum current density by a factor of only 1.8, so that ions must be supplied by ionization of the residual gas. For an arc like that of Fig. 3(b) (1 amp. maximum current, 1×10^{-6} sec. duration, and 5×10^{-3} mm Hg pressure) calculations indicate that the number of molecules entering the electron stream, assuming it to have the same breadth as the cathode spot, is of about the right size to provide sufficient ionization. At higher applied voltages and lower inductances, however, arcs have been produced with maximum currents much larger and lasting much shorter times, and it appears that the ionization produced (if the electron stream is no larger than the cathode spot) is orders of magnitude too small. Perhaps the arc can start at small current, small diameter, and high voltage, and then expand rapidly in size and current, with a rapidly decreasing voltage. Some evidence supporting this theory is found in Fig. 3(a), which shows the arc voltage decreasing throughout the arc's lifetime.

During the course of this work the author received many valuable suggestions from L. H. Germer, to whom he expresses sincere thanks.

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[12] I. Langmuir, Phys. Rev. 33, 954 (1929).

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On the Symmetry of Graphite

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X-ray diffraction evidence indicates that the symmetry of graphite can be no higher than twofold. Evidence consists of twin observations and the occurrence of satellite reflections, both of which are incompatible with sixfold symmetry. Both phenomena strongly suggest that the classical concept of equivalent carbon-carbon bonds must be discarded in favor of one involving unequal bond lengths and bond angles.

I. INTRODUCTION

RECENTLY, considerable interest has been shown in the conductivity and the band structure of graphite.[1–4] The theoretical studies and calculations have been based on the classical crystal structure determined by Bernal,[5] where the symmetry is considered to be hexagonal holohedral. The structure consists of planar sheets of carbon atoms arranged in equilateral and equiangular hexagonal rings. The atoms in the planes are separated by a distance of 1.42*kx* units and the planes by 3.348*kx*. Hexagonal symmetry is consistent with early x-ray diffraction studies and with most morphological examinations. Goldschmidt,[6] however, depicts a crystal which can have no higher than twofold symmetry. This is an isolated example and, apparently, has been regarded as a curiosity. Recently, Hoerni, and Weigle[7] have described extra reflections in electron diffraction patterns, which appear to double the *a*-axis. Finally, Pauling and the writer[8] have presented evidence based on certain twin relations which indicate a symmetry lower than hexagonal. It is the purpose of this communication to discuss this evidence and some of its implications, as well as to outline recently obtained x-ray diffraction data which appear to demonstrate conclusively that the symmetry of graphite cannot be higher than twofold. Although the study is not complete, it is felt that publication of the preliminary data is warranted because of its possible influence on theoretical studies.

II. TWIN OBSERVATIONS

Weissenberg and precession photographs, rotation and precession about the *c*-axis, have been taken of some hundred or more graphite crystals. These include

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* The Knolls Atomic Power Laboratory is operated by the General Electric Company for the AEC.

[1] C. A. Coulson, Nature **159**, 265 (1947).

[2] R. P. Wallace, Phys. Rev. **71**, 265 (1947).

[3] D. Bowen, Phys. Rev. **76**, 1878 (1947).

[4] S. Mrozowski, Phys. Rev. **77**, 838 (1950).

[5] J. D. Bernal, Proc. Roy. Soc. (A) **106**, 749 (1924).

[6] V. Goldschmidt, *Atlas der Kristallformen* (Carl Winter's Universitatbuchhandlung, Heidelberg, 1915), Vol. IV.

[7] J. Hoerni and J. Weigle, Nature **164**, 1088 (1949).

[8] J. S. Lukesh and L. Pauling, Am. Mineral. **35**, 125 (1950). Read before the Crystallographic Society of America, Ann Arbor, Michigan, April 7, 1949.

natural material from six localities as well as that produced synthetically during the pouring operation at an iron blast furnace. The common characteristic of all the crystals is lack of singularity. With few exceptions, all showed two or more individuals with a common *c*-axis. It was at first believed that this phenomenon was a result of the loose bonding between layers and had no structural significance. However, the fact that certain angular relations appeared with such frequency as to eliminate coincidence made it evident that there must be structural control. Several such relations were observed but, for the purpose of this discussion, attention will be focused on one which relates the individuals by approximately two and one-half degrees. This relation has been found in specimens from all localities studied; in those separated from clear, white calcite found in Low Township, Quebec, it has been found in nearly fifty percent of the crystals. It would appear, therefore, that this phenomenon is not an unusual one but is the rule rather than the exception. Examples of this twin relation are shown in Figs. 1 and 2 illustrated by *c*-axis precession photographs. In both cases, the "a" illustrations show the photograph as taken; several twin laws are evident. In the "b" illustrations, all diffraction spots except those belonging to the twin pair under consideration have been blocked out for clarity.

An angular relation of two and one-half degrees is difficult to rationalize on the basis of a structure con-

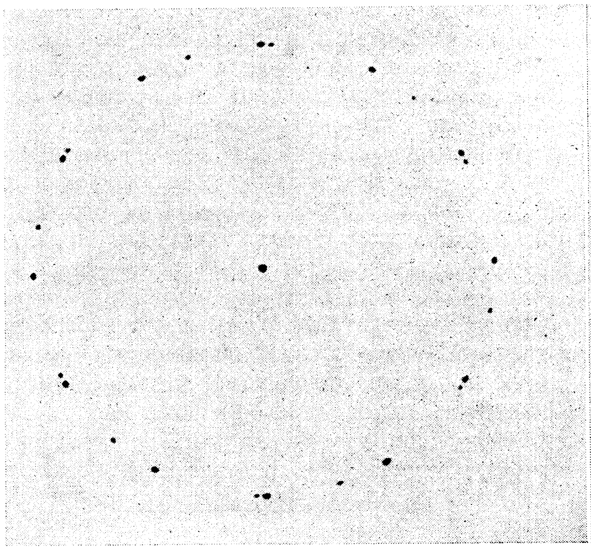

FIG. 1(a). 0-level, *c*-axis precession photograph of graphite, copper $K\alpha$-radiation, illustrating twinning. Crystal from Bouthillier Township, Labelle County, Quebec.

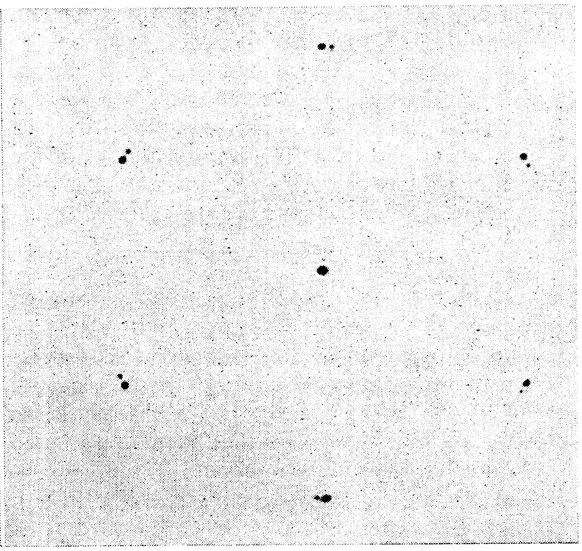

FIG. 1(b). Same as Fig. 1(a) with all individuals other than the pair separated by rotation of two and one-half degrees masked out.

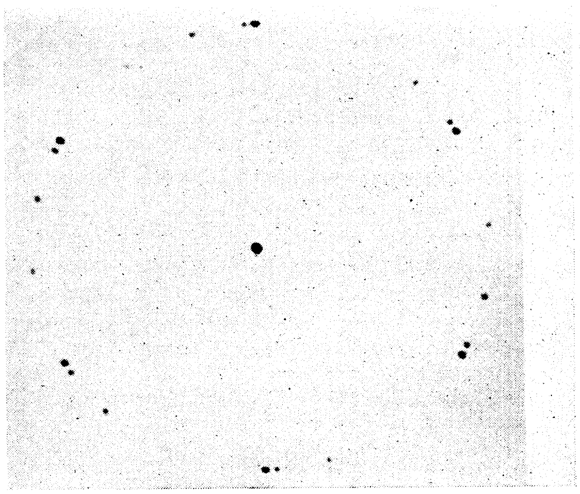

FIG. 2(a). Same as Fig. 1(a). Crystal from Low Township, Quebec.

FIG. 2(b). Same as Fig. 1(b). Crystal from Low Township, Quebec.

sisting of equiangular and equilateral hexagonal rings of carbon atoms. For this reason, the writer was led to postulate a non-equivalence of the three carbon to carbon bonds of each carbon atom. Only by destroying the regularity of the hexagon could a mechanism be found which would permit such a relation, and this, of course, degrades the symmetry.

Non-equivalence of bonds in a resonating system is consistent with the recent suggestion of Pauling[9] where he has shown that, in such a system, bond numbers tend to be a simple rational fraction with a preference for one-half. In the case of graphite, this would give, ideally, one bond of order one-half and two of one-quarter. To conform with the lattice dimensions, each carbon atom in the hexagonal ring would be required to have two bond angles of approximately 121° and one of about 118°, a sufficient departure from 120° to permit individuals to be related by the observed amount. Because of the loose bonding between layers, the short bond could well change direction from one layer to the next and thus alter the orientation of the remainder of the crystal. A full interpretation of this will not be possible without further structural study.

III. DIFFRACTION SYMMETRY

The precession photograph[10] gives an undistorted representation of the reciprocal lattice, and thus a true representation of the diffraction symmetry. The *c*-axis projection of the reciprocal lattice of graphite should display sixfold symmetry if the classical structure is the correct one. In all specimens that have been studied the reciprocal lattice points representing the conventional hexagonal lattice show complete sixfold symmetry. However, in a majority, if not all, of the cases there is evidence of a superstructure which has only twofold symmetry. This is shown in Fig. 3 which is the *c*-axis zero level of the reciprocal lattice, taken by the precession method, of a naturally occurring graphite crystal found in calcite from Gatineau County, Quebec. The radiation employed was copper $K\alpha$, filtered through nickel foil. Because of the small size of the simple, conventional, cell, only the 1010 group of reflections appears. It will be noted that two individuals are present. In Fig. 3b diffraction spots due to one individual have been masked out in order that the symmetry of the satellite reflections of the other individual may be seen more clearly. It is important to note that satellites occur associated with only four of the six hexagonally equivalent reflections and that these are so disposed as to be related by mirror planes rather than by axial rotation. Clearly the symmetry of the satellites can be no higher than twofold. A similar set of satellites appears on the first level. The same distribution of extra reflections has been found in natural samples from six localities as well as a synthetic one collected at a blast furnace. Figure 4 is an electron diffraction photograph of a flake of Ceylon graphite approximately 800A thick. It was kindly sent to the writer by Professor Jean Weigle of the University of Geneva. The same twofold distribution of satellites can be seen. From this universal occurrence it can be deduced that the phenomenon is not a result of distribution of impurity atoms or previous history of the sample.[11] Even if it were, the controlling factor in, say,

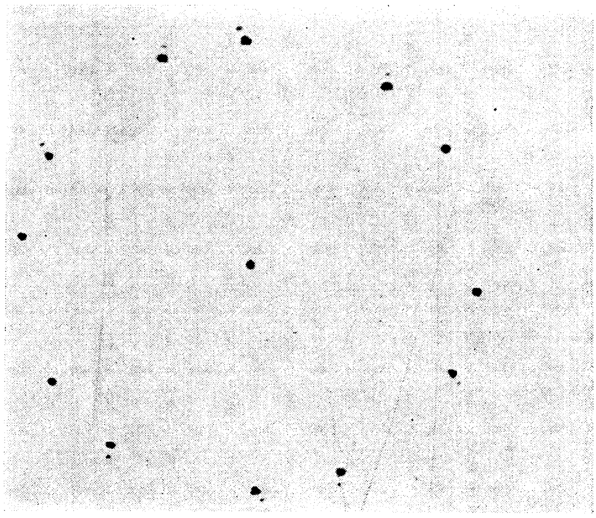

FIG. 3(a). 0-level, *c*-axis precession photograph of graphite, copper $K\alpha$-radiation, illustrating satellite reflections. Crystal from Gatineau County, Quebec.

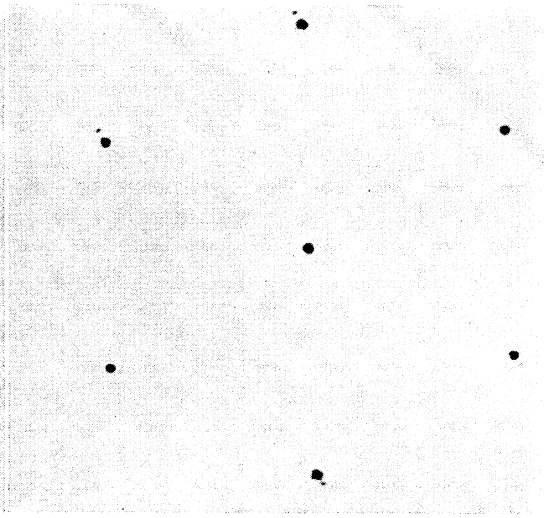

FIG. 3(b). Same as Fig. 3(a) with one twin individual masked out.

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[9] L. Pauling, Proc. Roy. Soc. (A) **196**, 23 (1949).

[10] M. J. Buerger, "The photography of the reciprocal lattice," ASXRED Monograph No. 1 (1944).

[11] Examination of Figs. 1 and 2 does not reveal the existence of the satellite reflections. They are, however, present on the original film but were lost in the photographic reproduction, which was designed to emphasize the twinning.

the arrangement of impurity atoms would necessarily be symmetry of the graphite itself and one would expect a hexagonal array of satellite reflections were the symmetry hexagonal.

A further point of very considerable importance is that the spacing (in direct space) represented by the distance between the satellite reflection and its parent is exactly thirty times that between the parent and its hexagonally equivalent reflection at 120°. This leads to an increase in the hexagonal a_0 of 15 times, if one assumes the existence of a superstructure. The unit cell then becomes, compared with the orthohexagonal cell of the classical structure

Orthohexagonal (classical)	Orthorhombic (new cell)
$a_0 = 2.456kx$	$a_0 = 36.840kx$
$b_0 = 4.254$	$b_0 = 4.254$
$c_0 = 6.696$	$c_0 = 6.696$

or, transforming axes to the more conventional form,

$$a_0 = 4.254kx$$
$$b_0 = 36.840$$
$$c_0 = 6.696.$$

Because of the scarcity of data concerning the distribution of the superstructure reflections it is not possible to assign a space group. However, those reflections which are present appear to conform to a symmetry not higher than $D_{2h}^{23}-Fmmm$ and probably lower. It is to be emphasized that interpretation of the satellites as representing a superstructure is tentative. The important point is the obvious lack of hexagonal symmetry.

IV. DISCUSSION

The evidence cited in the preceding paragraphs can be explained only on the basis of a structure consisting of non-equiangular and non-equilateral carbon rings. The observed twin relation requires that the bond angles be other than 120°. The superstructure suggests a perturbation within the plane with a fifteen ring periodicity. (No evidence has been found that the atoms within a given sheet are not co-planar.) In order to explain these experimental observations, it is necessary to postulate non-equivalence of the three bonds of each carbon atom. It is because of the possible bearing of the non-equal bond lengths on the band structure and Brillouin zone pattern of graphite that these observations are presented at this time. X-ray diffraction data are, so far, inadequate to allow a determination of the nature of the departure of the crystal structure from the classical one.

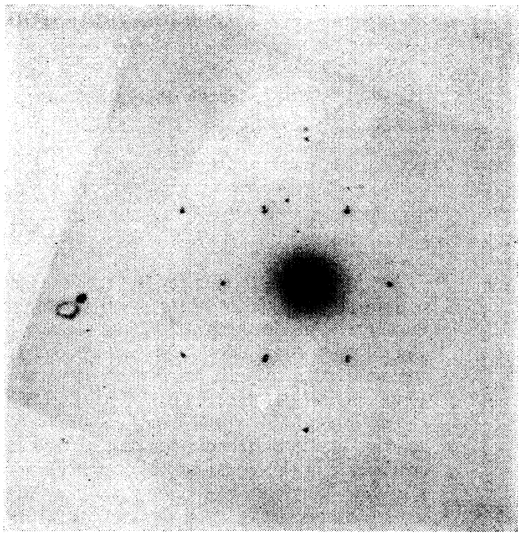

FIG. 4. Electron diffraction photograph of Ceylon graphite (courtesy Professor Jean Weigle).

It is of interest to note why the two observations described herein have not been reported before. The twinning cannot, of course, be detected in powder photographs. The reflections from the individuals of the twins are, further, superimposed in rotation photographs about the c axis and nearly so about other axes. The oscillation method, employed by Bernal[5] will not resolve them unless the oscillation range is of the order of one or two degrees. (The range normally employed is ten to twenty degrees.) The superstructure reflections are weak and can easily be overlooked in rotation and oscillation photographs. In regard to the powder method, the stronger satellite reflections are, coincidentally, superimposed on normal hexagonal reflections. For example, the reflection indexed on the basis of the new cell as $1\cdot 16\cdot 0$ has nearly the same spacing as $1\cdot 15\cdot 1$ ($10\bar{1}1$, hexagonal cell) and $1\cdot 14\cdot 1$ has a d value nearly identical with $1\cdot 15\cdot 0$ ($10\bar{1}0$, hexagonal cell).

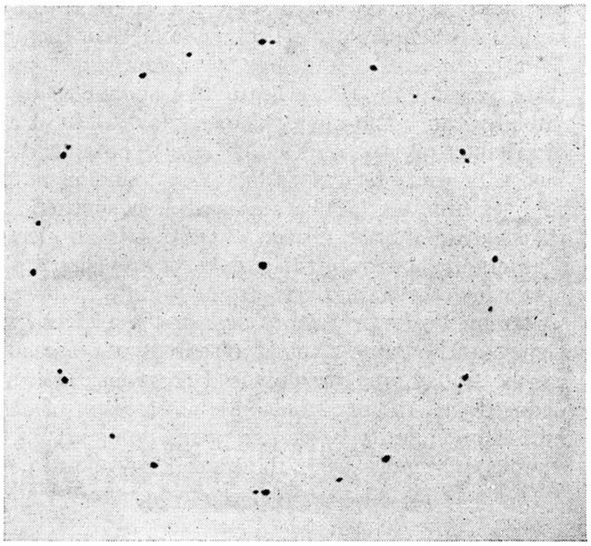

FIG. 1(a). 0-level, *c*-axis precession photograph of graphite, copper $K\alpha$-radiation, illustrating twinning. Crystal from Bouthillier Township, Labelle County, Quebec.

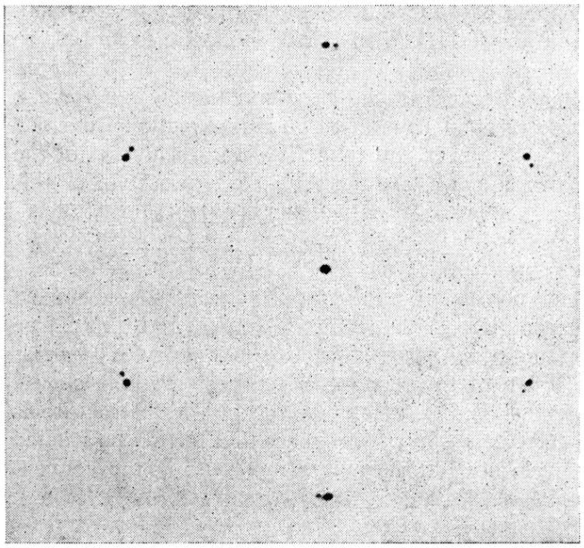

FIG. 1(b). Same as Fig. 1(a) with all individuals other than the pair separated by rotation of two and one-half degrees masked out.

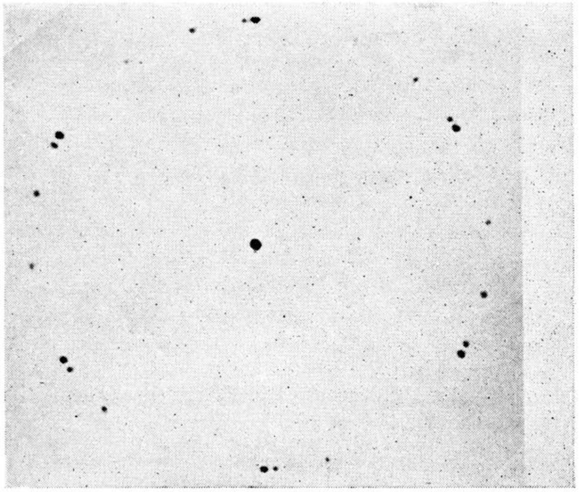

FIG. 2(a). Same as Fig. 1(a). Crystal from Low Township, Quebec.

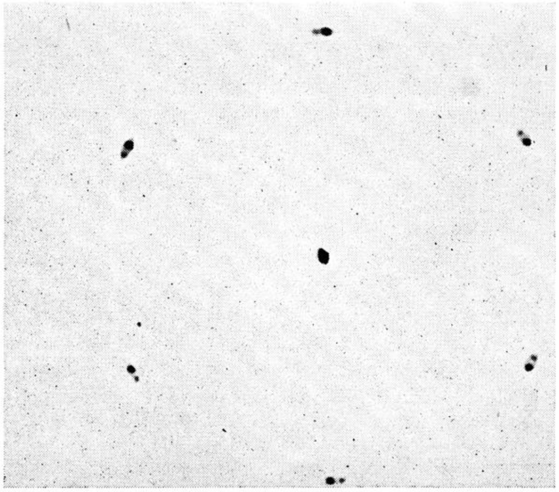

Fig. 2(b). Same as Fig. 1(b). Crystal from Low Township, Quebec.

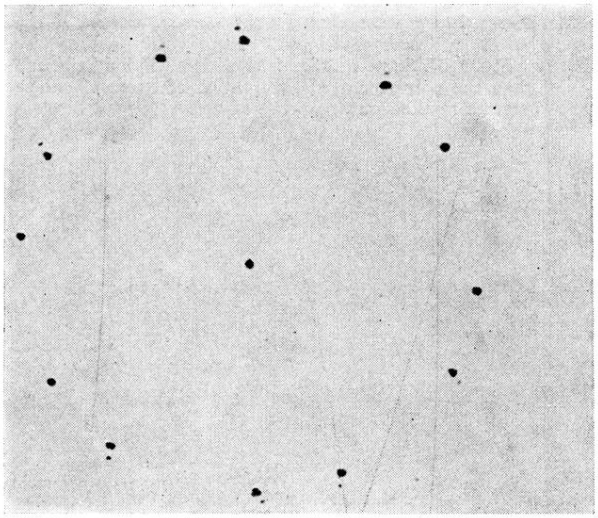

FIG. 3(a). 0-level, c-axis precession photograph of graphite, copper $K\alpha$-radiation, illustrating satellite reflections. Crystal from Gatineau County, Quebec.

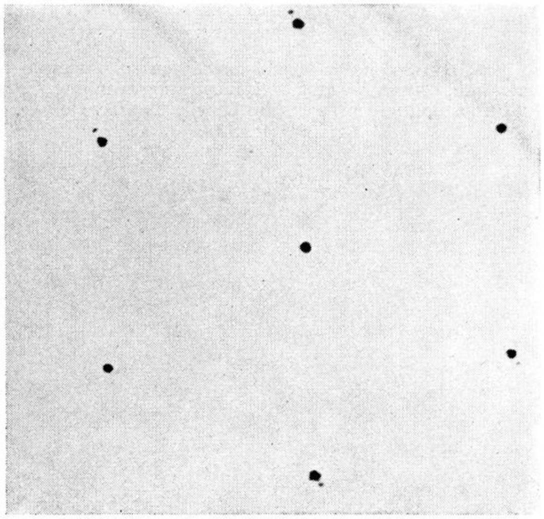

FIG. 3(b). Same as Fig. 3(a) with one twin individual masked out.

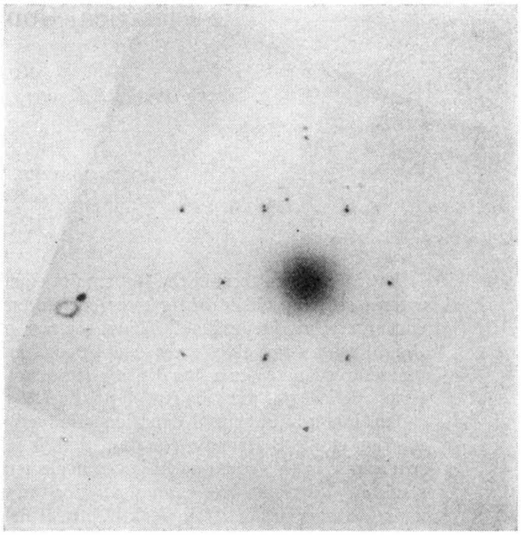

FIG. 4. Electron diffraction photograph of Ceylon graphite (courtesy Professor Jean Weigle).