X-ray studies of synthetic diamonds.

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(With Plates IX and X.)

[Read 2 April 1959.]

Summary. Studies are described of various specimens of diamonds made by the General Electric Company of New York, and by Allmänna Svenska Elektriska Aktiebolaget, Västeras, Sweden. The G.E. synthetic diamonds always contain single crystal inclusions of nickel or of a Ni-rich face-centred cubic compound. These are strictly parallel to the diamond surrounding them. If the nickel inclusions are twinned on (111), the diamond is similarly twinned; and this is usually the case. It is suggested that epitaxial growth is part of the mechanism of the graphite-to-diamond transformation in the G.E. technique. Other powdered or single-crystal inclusions are also found; some of those correspond to compounds that occur in meteoritic carbon. There is no parallel growth in such cases. The Swedish synthetic diamonds do not contain nickel, but they are generally less well-crystallized than the G.E. specimens. Both, however, give good diffraction spots indicating a well-ordered structure with (except very rarely) no trace of graphite present.

THIS work may be grouped under three headings: studies of diamonds made by the General Electric Company of New York, U.S.A. (hereafter referred to as G.E. diamonds); studies of diamonds made by the Allmänna Svenska Elektriska Aktiebolaget, Västeras, Sweden (ASEA diamonds); and a further study of a Hannay diamond.

The work is not as complete as we would have liked, but it seems possible that further investigation would be a waste of time, since presumably studies at present classified as secret will eventually be released for publication.

G.E. DIAMONDS.

These diamonds have been obtained from three sources: those that one of us (H. J. M.) was kindly allowed to select during a lecture visit to the G.E. Research Laboratories, Schenectady, New York; those sent from the G.E. Research Laboratories to various research centres in

Great Britain, including our own; and those sold in the U.S.A. and given to us by Mr. P. Neven of the Impregnated Diamond Products Ltd., Gloucester.

The diamonds are formed at pressures up to 100 000 atm. and temperatures up to 3000° K. The G.E. Research Information Services released a press statement 'Man-Made Diamond' in February–March 1955 containing articles by F. P. Bundy, H. T. Hall, A. L. Marshall, A. J. Nerad, H. M. Strong, and a résumé of the scientific literature of diamond making. A further article (Bundy *et al.*, 1955) made it clear that in addition to high pressures and temperatures, maintained over a controllable period of time in a 1000-ton press, certain 'chemical conditions' were also involved in the process of manufacture. At the time of writing, further details are still classified. In October 1957 the G.E. announced that up to that date they had made 100 000 carats of diamond powder and expected to make over 1 000 000 in 1958, the current price then being \$3.48 per carat, as against about \$2.80 per carat for corresponding natural diamond grit. The 24 % higher price for synthetic diamond seems not to be a deterrent to their sale, however, because the grinding efficiency of the synthetic diamond is said to exceed that of natural diamond by 35 %. We believe that this may be because the natural diamond grit contains cleavage splinters (C. B. Slawson, 1957) whereas the man-made diamonds, though largely irregular fragments, are comparatively uniform and are mostly twinned. The largest stone announced by G.E. measured about 1·2 mm. in its longest dimension. None of those available to us measured more than about $\frac{1}{3}$ mm. Very few were colourless; they were mostly a dirty white, grey, or brown, and badly shaped, but there was occasionally a green or yellow specimen tending towards an octahedral habit, and sometimes fairly well-formed black specimens consisting of parallel cubes were found. We are informed that reproducible variations of colour and habit can now be obtained and that, in particular, batches consisting almost entirely of cubes with good faces can be made to order. It is said to be difficult, though it is possible, to deposit diamond on a diamond seed. Gem-quality crystals have not been reported.

X-ray examination.

X-ray studies have included random rotation photographs, followed by Laue, rotation, and Weissenberg photographs of orientated single and twinned specimens from various sources, using Cu-$K\alpha$ and β, Mo-$K\alpha$, Cr-$K\alpha$, and Ni-$K\alpha$ radiation. Powder and single (including twinned) crystal photographs of natural diamond have been taken for comparison purposes.

Random rotation photographs taken with unfiltered Cu-K radiation showed the normal diamond pattern but, in addition, every G.E. diamond examined showed reflections in the 200 position that would not be expected for diamond, together with satellite spots on the high-angle side of all the diamond reflections (pls. IX and X). These satellite reflections were found to form the pattern of a face-centred cubic structure having a lattice constant of 3·539 Å. as compared with 3·567 Å. for the diamond (H. J. Grenville-Wells and K. Lonsdale, 1958*a*). The latter spacing is identical with that for natural diamond and no variation has been observed greater than the limit of experimental error, ±0·1 %. The density of G.E. diamond as measured by flotation of individual crystals in diluted Clerici solution is 3·517 g./c.c. at room temperatures, which is very close to the natural diamond calculated value of 3·514. There are, however, some G.E. diamonds which float in methylene iodide (density less than 3·3 g./c.c.) and yet give an X-ray pattern of normal lattice constant. The cause of this very low density has not been found but may simply be cracks; if it were due to vacant sites randomly arranged in the structure, these would be expected to show up as a strong background intensity, which is not observed.

Orientated rotation photographs confirmed the parallelism of the diamond and satellite structures. All such photographs showed the satellite structure, although with varying relative intensity; there were never any satellite spots in positions other than those given by a structure absolutely parallel to the diamond. These satellite spots are also, in general, as sharp as those of the diamond except that there is a small $\Delta\theta$-broadening at high angles, indicating that the satellite inclusions are under uniform strain. Occasionally the satellite spots are a little more drawn-out along constant-θ arcs than those of the diamond but if the diamond spots show the presence of variable orientation, then the satellite spots invariably do so also. A particularly interesting feature is shown in pl. IX, fig. 4, where the 222 'forbidden' diamond reflection appears accompanied by an even stronger 222 satellite spot.

Weissenberg photographs further confirmed the parallelism of the diamond and satellite structures and provided some intensity data. Using Mo-K radiation the satellite structure is not apparent except for the 200, 420, and other forbidden reflections, because the lattice constant is such that its satellite reflections coincide with those of the Kα_2 components of the diamond spots.

There are *alternative explanations of the satellite spots.* The first is that they are due to a structure that is geometrically cubic of side 3·54 Å. but of rhombohedral symmetry only, and is intermediate between diamond and rhombohedral graphite (fig. 1), having carbon atoms in positions

$$000,\ 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{2}0\tfrac{1}{2},\ \tfrac{1}{2}\tfrac{1}{2}0 \pm \left|\tfrac{1}{6},\ \tfrac{1}{6},\ \tfrac{1}{6}\right|$$

and therefore closely related to the diamond structure

$$000,\ 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{2}0\tfrac{1}{2},\ \tfrac{1}{2}\tfrac{1}{2}0 \pm \left|\tfrac{1}{8},\ \tfrac{1}{8},\ \tfrac{1}{8}\right|$$

being derived from it by a straightening of the carbon atom layers parallel to one set of (111) planes only (cf. N. Nath, 1935, H. Lipson, and A. R. Stokes, 1942). The relationship to the rhombohedral graphite

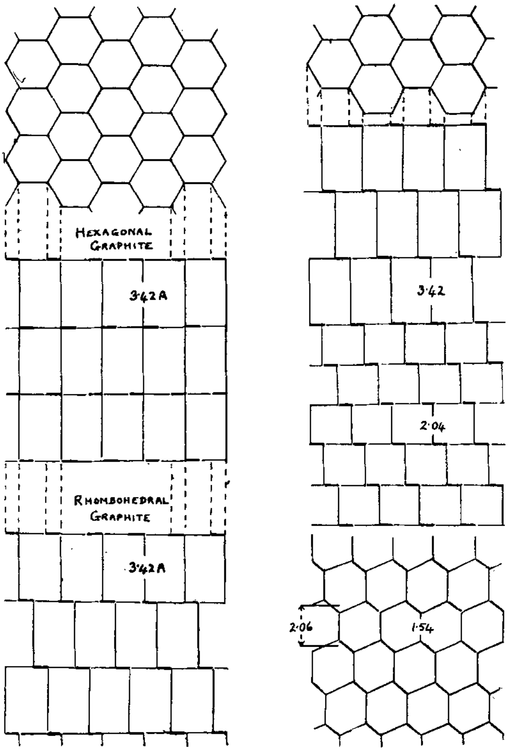

FIG. 1. Diagram to show the relationship between hexagonal and rhombohedral graphite and the possible transition from rhombohedral graphite through an intermediate structure to diamond (Grenville-Wells and Lonsdale, 1958*a*).

structure would be that the [111] axis would have been compressed to a length of 6·11 Å. instead of the normal 10·26 Å., the graphite layers thus being 2·04 Å. apart instead of 3·42 Å. This 'intermediate structure' would have structure factors:

$$\begin{aligned} \mathrm{F}(hkl) &= 8 f_c \cos \pi\,(h+k+l)/3 \\ &= 8 f_c \text{ if } h+k+l = 3n, \quad \text{but } 4 f_c \text{ if } h+k+l = 3n \pm 1. \end{aligned}$$

Thus the intensity of the 111, $\bar{2}20$, $31\bar{1}$, &c. reflections should be four times as great as that of $\bar{1}11$, 200, 220, 311, $\bar{3}11$, &c. In other words, the 200 reflection should be relatively weak compared with other satellite spots. In fact it is relatively strong (table I); but this does not rule out the possibility that such a structure may contribute to the satellite intensities. It cannot wholly explain them.

The second possibility is that the satellite structure is that of Ni or of some Ni-rich compound. β-Ni has a face-centred cubic structure of lattice constant 3·523 Å. at room temperatures and pressures; its value at the high temperatures and pressures used is not known to us. Ni is not normally an impurity in natural diamonds. Spectrographic analysis shows, however, that it is present in all the specimens of G.E. diamonds that we were able to send for examination and present in considerable quantity in the G.E. diamonds sold for industrial purposes, even after cleaning treatment designed to remove extraneous impurities (see Appendix). That the satellite spots are due to β-Ni alone is not possible because of the strength of the 200 reflection (table I), but that they are due to a Ni-rich compound can easily be proved by taking X-ray photographs with various incident radiations. The linear absorption coefficients of C and Ni respectively for the incident radiations used are as follows:

	Mo-$K\alpha$	Cu-$K\beta$	Cu-$K\alpha$	Ni-$K\alpha$	Cr-$K\alpha$
C ...	2	12	16	23	53
Ni ...	430	2640	430	530	1220

Those of carbon containing a small percentage of nickel and of nickel surrounded by a carbon matrix will differ slightly but not appreciably from these values (H. J. Grenville-Wells and K. Lonsdale, 1958*b*). It was found that the 200 satellite spots, which are the most easily observed, are relatively strong (compared with the diamond spots) for Mo-$K\alpha$ but weak for Cr-$K\alpha$. The most convincing evidence, however, is obtained from an X-ray tube having a copper target contaminated with nickel. The amount of contamination is such that the Ni-$K\alpha$ and Cu-$K\beta$ spots, which are at approximately equal distances on each side of the Cu-$K\alpha$ reflection, are of comparable intensities. The relative intensities for various diamond reflections for the three wave-lengths 1·66 Å. (Ni-$K\alpha$), 1·54 Å. (Cu-$K\alpha$), 1·39 Å. (Cu-$K\beta$) give mean values for the proportions in the incident radiation as follows:

$$I_0(\text{Ni-}K\alpha):I_0(\text{Cu-}K\alpha):I_0(\text{Cu-}K\beta) = 9:100:16.$$

The Ni-$K\beta$ spots were, in general, too weak for observation, but were in any case not needed; W-L spots were also present, due to tungsten contamination, but were not used.

The observed values of the satellite spot intensities, normalized to the Cu-$K\alpha$ 200 intensity, are given in Table I. As will be seen, the Cu-$K\beta$ intensity is markedly weakened (filtered out) relative to the Ni-$K\alpha$. This definitely proves the presence of Ni in the subsidiary structure, and the actual intensities, together with the sharpness of the satellite spots, can be used to give an approximate idea of the size of the inclusions, which appear to be of the order of 5.10^{-4} cm. linear dimensions (H. J. Grenville-Wells and K. Lonsdale, 1958*b*). The G.E. diamonds, when examined at high magnification, are seen to contain so much impurity and other irregularities that it is not possible to verify the presence of these nickel-rich inclusions visually.

TABLE I. Observed ratios of satellite spot intensities, taking the Cu-$K\alpha$ 200 spot as 100, compared with the ratio of incident intensities, I_0.

	111	200	022	311	222	400	133	420	422	I_0
Ni-$K\alpha$	5·0	9·4	3·0	2·9	1·6	0·4	..	..	..	9
Cu-$K\alpha$	53·8	100	36·0	25·4	15·5	9·6	8·8	16·0	..	100
Cu-$K\beta$	1·4	5·4	0·7	1·0	0·6	0·4	..	..	..	16

We have previously suggested that the subsidiary structure may consist of the cubic form of $\text{Ni}_x\text{C}(x > 4)$ reported by R. Bernier (1951).[1] If this is so, the intensities observed would indicate some randomness of both Ni and C in a structure having a partial rock-salt type character. Attempts to repeat the synthesis of cubic Ni_xC for intensity-comparison purposes have not been successful but in any case the inclusions in the G.E. diamonds may have been formed under conditions of high pressure and temperature not reproducible in an ordinary laboratory.

Some surprise had been felt that so small an amount of Ni as 0·2 % should give easily visible diffraction spots. A mixture of diamond and Ni powder was therefore made in as near this proportion as was possible. The X-ray pattern of this mixture did indeed show the Ni lines quite

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[1] Distances given in this paper as Å. are really kX; to correct to Å. multiply by 1·00202.

clearly (pl. IX, fig. 5). The diffraction effect of the impurity would be expected to be even clearer where it is concentrated into a few single crystals.

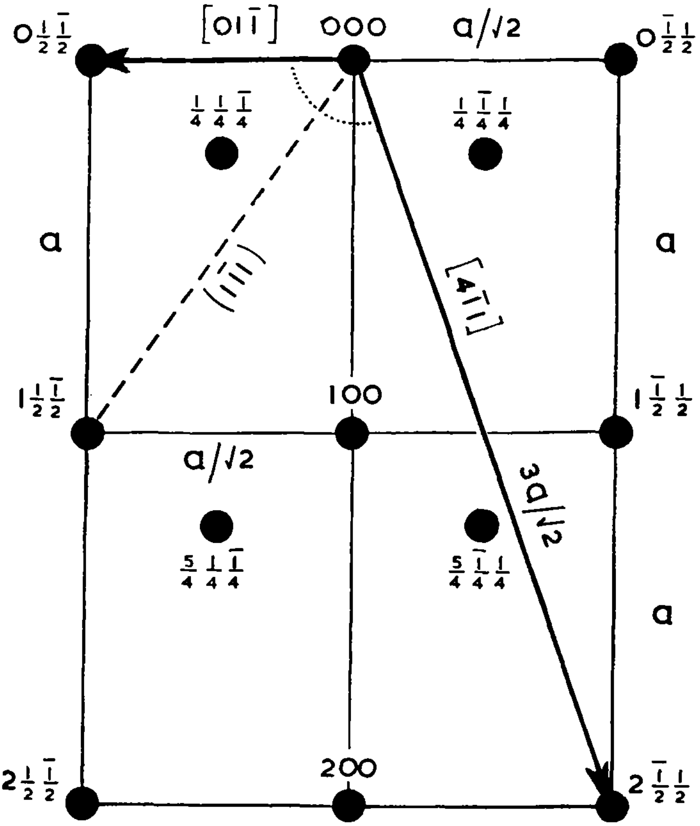


FIG. 2. The axis $[01\bar{1}]$, identity period $a/\sqrt{2}$, twins across $(1\bar{1}1)$ into $[4\bar{1}1]$, identity period $3a/\sqrt{2}$. The positions of carbon atoms actually lying in the (011) plane through the origin are shown. Compare table II and pl. IX, figs. 1–4 for the reflection spots found for a rotation about $[01\bar{1}]$ and $[4\bar{1}1]$ of a twinned crystal.

The G.E. diamonds are almost invariably twinned on (III), although the components may be of very unequal magnitudes. Whatever the degree of twinning, it seems to be paralleled by the Ni-rich inclusions which are also, in that case, twinned on (III). Pl. IX, figs. 1–4 show this very clearly. The diamond was set to rotate about a $[01\bar{1}]$ edge. The layer lines on the photograph so obtained correspond to an identity distance of $3a/\sqrt{2}$ instead of to $a/\sqrt{2}$, ($a = 3{\cdot}567$ Å.). The first and second layer lines, which are due to one member of the twin only, may be of weak intensity compared with the zero and third layer lines, for both diamond and Ni structures. Fig. 2 shows that the $[01\bar{1}]$ reflects across $(1\bar{1}1)$ to coincide with $[4\bar{1}1]$. The reflections occurring on the various layer lines will be as shown in table II (those due to the twin rotating about $[4\bar{1}1]$ are underlined). A pattern of this kind (with 200 absent) can of course be obtained from a natural diamond twin. The point to be emphasized here is the exact parallelism in the intensity distribution as well as in spot positions for the G.E. diamond and Ni structures. We have here a twinned inclusion within a twinned diamond, the twin law and the approximate proportions of the individuals being the same in each case. It is a significant fact that no trace of *free* Ni has been found by X-rays and that the G.E. diamonds are strongly attracted by an electromagnet (B. W. Anderson, 1958). They do not appear in general to give X-ray fluorescence in a Cu-$K\alpha$ incident beam and this confirms the comparative absence of iron shown by the spectrographic analysis (but see below, p. 196). The general fluorescence of a random sample in ultra-violet light is surprisingly normal.

TABLE II. Indices of the spots observable on an X-ray diffraction photograph of a twinned crystal rotating about $[01\bar{1}]$ of one member of the twin; this is $[4\bar{1}1]$ of the other. Indices for the second member underlined.

$k-l = 2$	$11\bar{1}$	020	220	131 $31\bar{1}$	—	—	331 $3\bar{1}\bar{3}$
	$\bar{1}1\bar{1}$	$00\bar{2}$	$20\bar{2}$	$\bar{1}31$ $\bar{3}1\bar{1}$			$\bar{3}31$ $\bar{3}1\bar{3}$
	$\underline{1\bar{1}1}$	—	$\underline{220}$	$\underline{1\bar{3}\bar{1}}$	—	—	—
$\underline{4h-k+l} = 6$			$\underline{20\bar{2}}$				
$\underline{4h-k+l} = 4$	$\underline{111}$	—	$\underline{0\bar{2}2}$	—	$\underline{22\bar{2}}$	$\underline{004}$	$\underline{133}$
	$\underline{1\bar{1}\bar{1}}$					$\underline{0\bar{4}0}$	
$\underline{4h-k+l} = 2$	$\underline{11\bar{1}}$	$\underline{002}$	—	$\underline{131}$	—	—	—
		$\underline{0\bar{2}0}$		$\underline{1\bar{1}\bar{3}}$			
$k-l = 0$	111 $\bar{1}11$	200	022	311 $\bar{3}11$	222 $\bar{2}22$	400	133 $\bar{1}33$
	$\bar{1}\bar{1}\bar{1}$ $1\bar{1}\bar{1}$	$\bar{2}00$	$0\bar{2}\bar{2}$	$\bar{3}\bar{1}\bar{1}$ $3\bar{1}\bar{1}$	$\bar{2}\bar{2}\bar{2}$ $2\bar{2}\bar{2}$	$\bar{4}00$	$\bar{1}\bar{3}\bar{3}$ $1\bar{3}\bar{3}$
	—	—	$\underline{022}$	$\underline{13\bar{1}}$	—	—	—
$\underline{4h-k+l} = 0$			$\underline{0\bar{2}\bar{2}}$	$\underline{\bar{1}\bar{3}1}$			

The graphite→diamond transformation would seem in the case of the G.E. process to depend upon the presence of this Ni-rich parallel inclusion. It is impossible to avoid the conclusion that the diamond has grown epitaxially upon the nickel. Fig. 3 shows that the structures of the octahedral planes of nickel and of diamond are closely similar in dimensions. The layer plane of graphite is similarly almost identical with the projection of the puckered hexagons of diamond $\{111\}$. A possible mechanism of transformation is shown in fig. 4. According to H. T. Hall (1958) the sequence of events in the high-pressure, high-temperature synthesis in the laboratory is as follows: the high pressure is first applied to the starting material; then, maintaining the high pressure, the material is subjected to a temperature sufficiently high to obtain a reasonable rate of transition or reaction (the pressure and temperature together being such that the end-product, which would be only metastable at NTP, is stable); next, the temperature is decreased to room temperature; and finally the pressure is decreased to atmospheric.

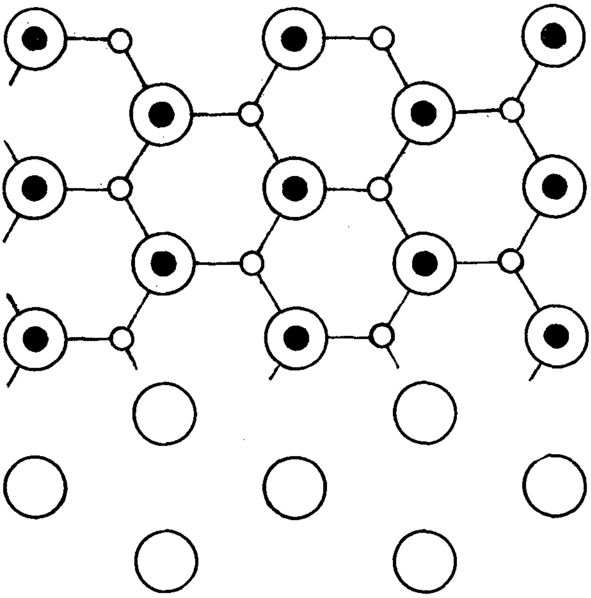
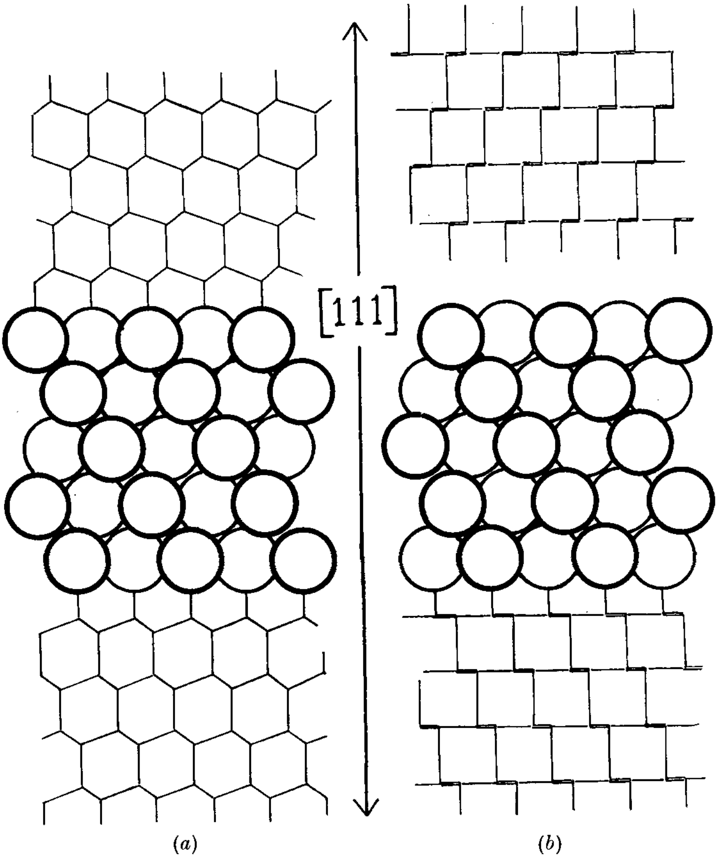


FIG. 3. Correspondence between (111) planes of diamond (or rhombohedral graphite) and of Ni or Ni_xC. Large circles: Ni atoms. Small circles: C atoms; one level for graphite, two levels for diamond.

In another publication H. T. Hall (1956) states that purely thermodynamic considerations 'indicate that diamond can not be formed directly from graphite. Experiment confirms this conclusion at pressures to 100,000 atmospheres and temperatures to approximately 3000° C.'

The sequence of events in the graphite→diamond transformation would seem to be: First, the high pressure brings the graphite layers much closer together, at the same time causing sideways shifts in favour of the rhombohedral form in which there is a repeat after three layers instead of after two as in the hexagonal form (see fig. 1; G. E. Bacon (1950) has proved that the hexagonal→rhombohedral graphite transformation may be brought about by mechanical working); when the graphite layers are pressed close to the octahedral face of a nickel grain, alternate carbon atoms attach themselves firmly to nickel atoms (the fact that nickel carbides can be formed shows that such bonds are



(*a*) (*b*)

FIG. 4*a* (*left*): Growth of diamond twin on Ni base. 4*b* (*right*): Graphite under pressure, in relation to the Ni base.

possible); or it may be that the attachment is to a surface carbon layer in a cubic form of Ni_xC, *if this exists prior to the experiment.* The imposition in the next stage of a high temperature, the high pressure being maintained, would have two possible effects: some carbon atoms might diffuse through the nickel grains to form Ni_xC, having a lattice constant slightly greater than that of pure cubic Ni; and the graphite layers would be violently agitated although they could not separate. Since each alternate carbon atom has attached itself to the Ni atoms in an octahedral face of the included Ni grains, only the unattached, intermediate carbon atoms would be free to move permanently out of the plane of the attached graphite layers. This could initiate the formation of diamond, the plane layers becoming puckered and the highly-compressed van der Waals bonds between layers becoming normal C–C diamond bonds. A lowering of temperature, pressure still being maintained, would stabilize the diamond structure at room temperature around the nickel inclusions, the reversion to graphite being prevented by the continued compression. The high pressure could then be safely reduced to atmospheric.

One important question that remains is how the parallelism of graphite (0001) layers and of the octahedral planes of the Ni-rich inclusions is achieved in the first place, and how such relatively large quantities of Ni can be absorbed and not show even greater filtering of the Cu-$K\beta$ component of the incident radiation. If the Ni inclusions were even approximately spherical and of radius 5.10^{-4} cm. the overall intensity of the satellite spots and the relatively high concentration given by the spectrographic analysis would both indicate that the number of parallel crystalline inclusions present in a diamond of radius 0·3 mm. must be of the order of twenty. Admittedly the presence of twinning makes the calculation difficult because the proportion and distribution of diamond contributing to the measured spot intensities is not precisely known, but it cannot be far wrong. Possibly the existence of the Widmanstätten patterns in nickel-iron meteorites gives a clue. In a strong magnetic field graphite will orientate itself with the layers of carbon atoms parallel to the lines of force. Nickel filings, on the other hand, or beads of molten Ni recrystallizing, would orientate themselves along the lines of force. Since it is necessary to begin with single crystal material it may be that the necessary parallelism is achieved magnetically, perhaps with some initial annealing of the nickel or nickel-rich crystallites in a magnetic field.

The suggestion that the nickel may be growing in cracks in the diamond structure does not explain the invariable parallelism, nor the need for nickel at all; and it also leaves the process of transformation unexplained. Since Ni is not found in natural diamonds, however, it cannot be essential to the process. Habit and colour will also depend upon the presence of traces of other impurities.

Inclusions in powdered form gave powder lines on a number of the specimens examined. None of these was identified. One of the G.E. diamonds sent to Birkbeck College, London, had exceptionally streaky Ni-satellite spots (indicating more disorientation than was normal for the inclusions). This also showed continuous powder lines corresponding to spacings 8·0, 3·68 Å., &c. Similar lines were found for a green octahedron from the University College batch, which was also the only G.E. diamond showing any trace of a diffraction line due to graphite. Similar lines had previously been observed from a natural diamond.

One University College specimen, consisting of a group of fairly well-formed parallel black cubes (not unlike cliftonite in appearance) agreed with a greyish-black granular fragment in the batch returned from spectrographic analysis 1 (see Appendix) in showing a strong line at 3·08 Å. and many others corresponding to smaller spacings. This black specimen showed a really remarkable parallelism between diamond and satellite spots (pl. X, fig. 1), the latter being very sharp indeed except at high angles. (Cliftonite has been studied by Grenville-Wells, 1952.)

One twin consisting of two interpenetrating cubes with excellent cube faces showed no inclusion except the usual Ni, but did give high background scattering with Cu-*K* radiation, which suggests the presence of iron. This is also common in Congo diamonds, the only natural source from which cube faces (usually imperfect) are frequently found.

Small foreign crystals were also found, associated with the diamonds in specimens supplied or purchased. None of these was identified. For example, among the G.E. diamonds sent to Birkbeck College was a somewhat flattened, badly-shaped octahedron with a black matt surface, which gave no diamond or Ni spots, but gave a powder pattern leading to interplanar spacings:

2·95 Å., *w*; 2·53, *ms*; 2·07, *w*; 1·72, *vvw*; 1·475, *ms*;
1·275, *w*; 1·085, *mw*; 1·00, *w*; 0·88, 0·855, &c., all *vvw*.

Some of these lines were also found from a red crystal, also not diamond, in a sample of G.E. diamonds sent to the Royal Institution, London. This red crystal also gave diffraction spots and some other high-spacing rings. These diffraction spots corresponded to the strongest spots from a yellow, poorly-shaped octahedron from the Birkbeck College sample and from a white transparent crystal from the University College batch, neither of them diamond. The strong spots from all these single crystals fitted the (0002) line of graphite at 3·4 Å., but the remaining spots were not identified and the agreement may be accidental.

The lines from the black matt octahedral crystal were identical with some found from several, but not all, samples of graphite from the Dayton (Ohio) meteorite, which we had obtained from the Smithsonian Institution, U.S.A. The significance of this agreement between the lines from impurities found among the several batches of G.E. diamonds and from meteoritic material is not known. Nor can we tell whether these extraneous materials were introduced as part of the process of manufacture, or during subsequent crushing and sieving of the synthetic diamonds. It is to be hoped that this information will be released eventually.

SWEDISH DIAMONDS.

A small sample of ASEA synthetic diamonds was sent to us through the good offices of Professor G. Hägg of Uppsala and by courtesy of Dr. H. Liander, who had announced their manufacture in an article in the 'ASEA Journal' (1955). The 11-year project had cost about 2 million marks and its success in February 1953 was due to the collaboration of Messrs. Liander, Liljeblad, Lundblad, v.Platen, and Wallin. Temperatures and pressures of up to 3000° C. and 70 000 kg./cm.^{2} were attained. The 12 000-ton press used was made of a new material (unspecified) and was of surprising capacity (500 c.c.). These diamonds are not yet on the market, but further experiments are being made.

The material sent us was not sufficient for a spectrographic analysis, and the individual crystals in our specimen were even smaller and more badly-shaped than those from the G.E. research laboratories. A random sample was formed into a 'powder' specimen and stationary, rotation, and oscillation photographs were taken of it. These showed the presence of a number of very small individual grains of diamond and a few additional powder lines or sections of lines not due to diamond. Separate grains were then set up for X-ray studies.

These separate diamond grains showed, in general, no sharp diffraction spots or lines other than those of diamond itself. It is clear that they do not contain Ni or any other crystallized inclusions. The possibility of impurity atoms within the diamonds is not eliminated by this method, but if so these are not in the form of even tiny crystals either aligned or not aligned with the diamond. There is no general fluorescent scattering such as would be expected with Cu-$K\alpha$ if iron were present (pl. X, figs. 3–5).

A small portion of the ASEA sample was cleaned with concentrated nitric and sulphuric acids. A subsequent 'powder' photograph still showed some extraneous powder lines which were subsequently identified as due to platinum, present as blackish grains in the specimen. The lines are sharp but fade off in intensity towards the back-reflection region, indicating that the Pt crystallites are large but with a considerable degree of static disorder. It was at first supposed that the Pt (lattice constant 3·92 Å.) might have been introduced as a catalyst in the original matrix and partially recrystallized subsequently. In a communication from Dr. Liander, however, he says: 'This platinum was not intentionally used as a catalyst. In some experiments we have used platinum-canned capsules for the containing of certain reaction mixtures. At the high temperature the platinum has melted and traces of platinum may, therefore, have been attached to these diamonds.'

Laue photographs of G.E. and ASEA diamonds gave no extra spots or streaks typical of 'type I' diamonds (cf. Lonsdale, 1942).

HANNAY DIAMONDS.

It seemed of interest to take a random rotation (Cu-$K\alpha$) photograph of one of the Hannay diamonds (F. A. Bannister and K. Lonsdale, 1943) to see whether any crystalline inclusions were present that would indicate that it must have been made in the laboratory. Pl. X, fig. 6, shows such a photograph. No trace of Ni lines can be seen, although there is one faint powder line present which could not be identified. The X-ray photograph shows that it is a very well-crystallized specimen, in no way distinguishable from a natural diamond. We are inclined to believe that it is a natural and not a synthetic diamond. One point may, however, be made. Hannay asserted that he put some lithium into his mixture. Although no lines due to lithium can be seen, it is a fact that lithium does have a lattice constant (3·509 Å.) close to that of diamond, and in spite of its being a body-centred and not a face-centred cubic structure, it might act as a substrate for the growth of diamond. Hannay, of course, could not possibly have been aware of this similarity of lattice constants, which was not discovered until many years after his death.

Appendix.

Spectrographic analyses have been carried out as follows:

A sample sent to us directly from the G.E. Research Laboratories, Schenectady, N.Y., was divided into three parts. One part was retained for X-ray analysis. Two samples, one larger than the other, were sent for spectrographic analysis to the Research Department of Messrs. Johnson Matthey and Co. Ltd., who supplied the information given in columns 1 and 2 of table III.

Two samples were given to us by Mr. P. Neven, Director of the Impregnated Diamond Products Ltd. One of these had been treated with a mixture of concentrated nitric and hydrochloric acids, followed by molten potassium hydroxide with the addition of potassium nitrate at about 400° C., and finally by a second treatment with aqua regia. As a result of this treatment there was a loss of weight of up to 1·5 %, but with no noticeable change in the dirty greenish-grey colour of the sample. The spectrographic analysis of a random portion of this sample is given in column 3 of table III. The second sample was entirely untreated, and the analysis of a random portion of this is given in column 4.

TABLE III. Spectrographic analyses of synthetic diamond.

	1. Larger sample from G.E. lab.	2. Smaller sample from G.E. lab.	3. Cleaned G.E. industrial	4. Original G.E. industrial
Nickel	0·2%	0·2%	3(±1)%	1(±0·3)%
Silicon	0·05	0·1	0·005	4(±1)
Aluminium ...	0·07	0·07	—	0·05
Iron	0·002	0·05	0·0002	0·0005
Manganese ...	0·003	0·005	0·002	0·002
Magnesium ...	0·002	0·01	0·005	0·002
Sodium	0·002	0·005	0·003	—
Potassium ...	0·005	0·005	—	—
Titanium ...	0·003	0·005	—	—
Calcium	0·002	0·01	0·005	0·003
Chromium ...	—	0·005	—	—
Copper	0·0002	0·004	0·0001	0·003
Boron	—	0·0005	—	—
Thallium ...	—	—	0·05	—
Silver	—	—	—	0·003

The following elements were tested for (if not mentioned in the table they were not present in detectable amounts): Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hg, In, Ir, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Rb, Rh, Ru, Sb, Si, Sn, Sr, Te, Th, Ti, V, W, Zn, Zr.

The fact that specimens 1 and 2 differ, although taken from the same sample, is a measure of the variability of the material. This is also shown by specimens 3 and 4, since one would expect that 4 should contain all the elements found in 3, as well as those (mainly Si) removed by the treatment, whereas thallium and sodium were found in the cleaned, but not in the uncleaned samples.

Some of the impurities found may have been added accidentally after the initia manufacturing process was completed. Our X-ray diffraction studies, for example, have shown the presence of some grains of copper as foreign bodies.

Acknowledgements. Our thanks are due to all those mentioned in the paper who supplied us with specimens or information; also to Drs. R. Mason and S. Chandrasekhar, who assisted with experimental measurements, and to Dr. H. Morrogh, who has made various nickel carbides for X-ray examination.

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Explanation of Plates IX and X.

Plate IX. Fig. 1. (*Top, left.*) Natural diamond twins rotating about $[01\bar{1}]$ and $[4\bar{1}1]$ (slightly mis-set). Cu-*K* filtered radiation. Compare table II.

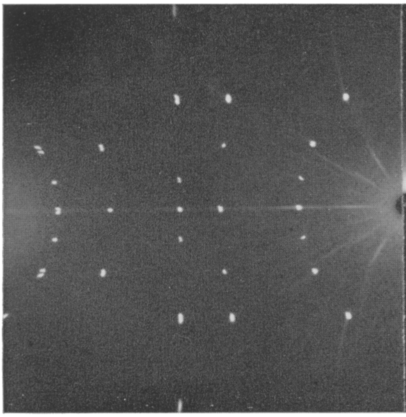
Fig. 2. (*Top, right.*) G.E. green diamond twins rotating about $[01\bar{1}]$ and $[4\bar{1}1]$ (slightly mis-set). Cu-*K* filtered radiation. Note satellite spots, especially those corresponding to 200, 002, and 020 on zero, first, and third layer lines, and their complete parallelism with the diamond matrix structure.

Fig. 3. (*Middle, left.*) Another G.E. diamond with weak twin spots. Strong Ni satellite spots at 200 and 020. The 002 twin Ni satellite spots are visible on the film but too weak to reproduce. Note the 222 doublet due to diamond and Ni (the latter being the stronger), and the 133 satellite.

Fig. 4. (*Middle, right.*) A single G.E. diamond with a strong single Ni satellite. Note the 222 doublet, and 133 satellite.

Fig. 5. (*Bottom.*) Upper half, left: Diamond powder+0·3 % Ni powder. Upper half, right: Diamond powder. Lower half: Ni powder. All taken with Cu-*K* filtered radiation: showing how Ni would give clear 200 and 420 reflections and satellites on the high angle side of all diamond reflections.

Plate X. Fig. 1. (*Top, left.*) Random rotation, with unfiltered Cu-*K* radiation, of grey-black granular G.E. diamond (part of specimen returned after spectrographic analysis). The Ni satellite spots are fairly strong and show some spreading along arcs. The 200 satellite spots show no $\Delta\theta$ broadening but the 420 satellite spots are broadened, giving evidence of strain. A powder inclusion gives a strong 3·08 Å. line.



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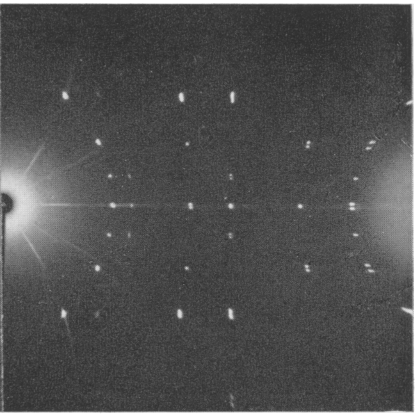

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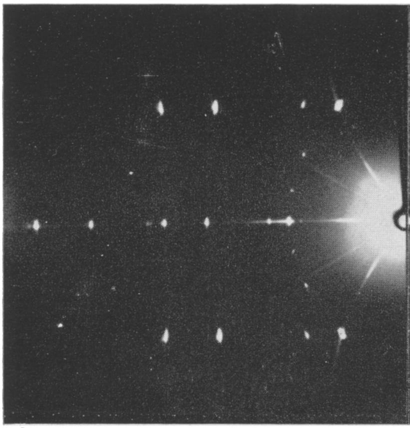

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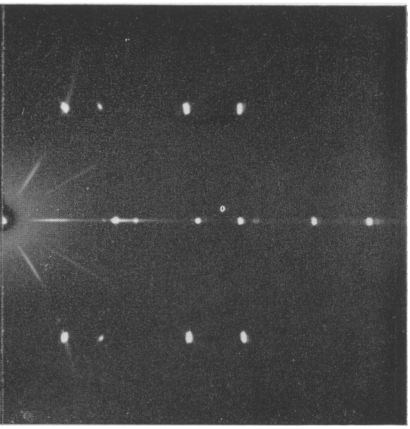

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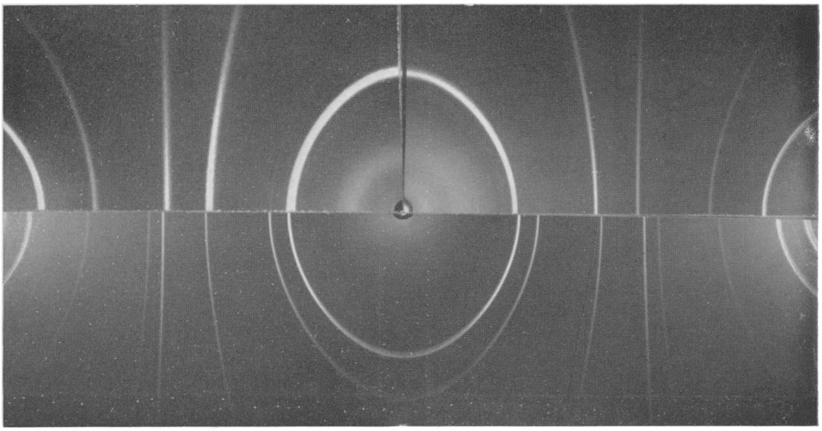

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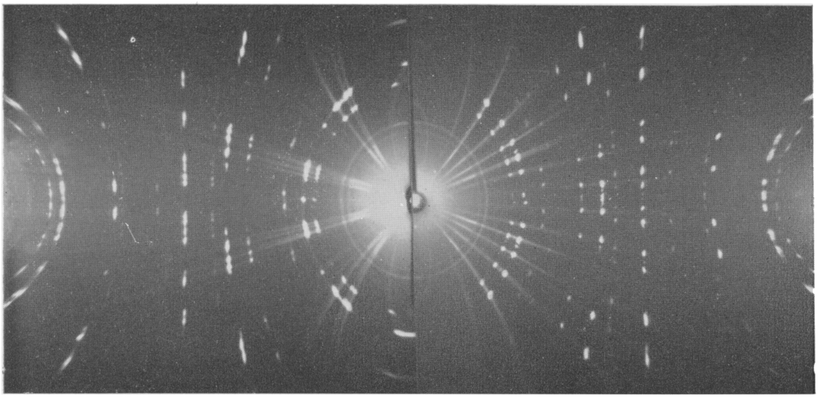

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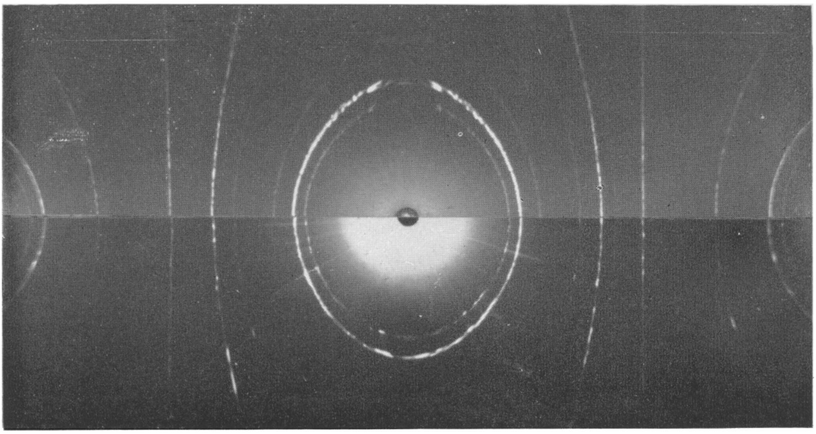

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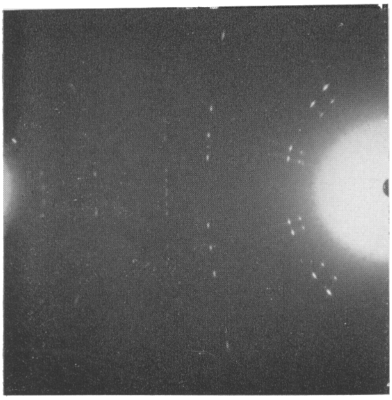

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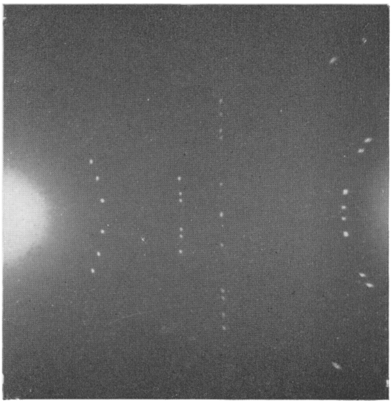

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FIG. 2. (*Top, right.*) The same powder inclusion line is found from another G.E. diamond, which consists of black parallel cubes. The Ni satellite spots do not spread along arcs.

FIG. 3. (*Middle, upper half.*) G.E. diamond, showing 200 Ni satellite lines.

FIG. 4. (*Middle, lower half.*) ASEA diamond; no satellite. Both specimens consist of randomly-orientated crystallites.

FIG. 5. (*Bottom, left.*) Random rotation of ASEA single diamond, Cu-K radiation.

FIG. 6. (*Bottom, right.*) Hannay diamond. Single crystal with no satellite, though the film shows a few weak powder lines which do not reproduce.