### 180.   *A Physicochemical Technique for Evaluating Defects in Graphite.*

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Threshold values of chemical potential are found, below which even well-oriented graphites fail to form crystal compounds by intercalation of iodine monochloride or bromine.   Such thresholds, measured by a titration method in which the end-point is determined by changes of electrical resistance, have been correlated with other data on defect structures in pyrolytic graphite. The defect concentrations have been varied by adjusting the conditions of pyrolysis and heat treatment.   Defects have also been introduced into some samples by fast-neutron bombardment, and the annealing behaviour of such defects has been correlated with the progressive displacement of the intercalation thresholds.   The mechanisms which operate at the onset of intercalation are discussed in the light of these findings.

WHEN the formation of crystal compounds by intercalation of halogens into graphite is followed by observations on the increase in thickness of specimens, by determinations of weight uptake, or by measurements of the decrease in relative electrical resistance, $R/R_0$, threshold concentrations are found below which no perceptible compound formation occurs.[1] These thresholds are found to be related quite closely to the characteristic defect structures studied in pyrolytic graphite by other means,[2] and this finding points the way to

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[1] Saunders, Ubbelohde, and Young, *Proc. Roy. Soc.*, 1963, *A*, **271**, 499, 512.
[2] Blackman, Saunders, and Ubbelohde, *Proc. Roy. Soc.*, 1961, *A*, **264**, 19.

a new technique for making systematic studies of defect structures in this class of solid by use of simple physicochemical measurements.

In the present experiments, changes of relative resistance have been followed rather than increase in thickness, because the electrical measurements can be conveniently made with greater precision. Specimens were immersed at constant temperature in solutions of bromine or iodine monochloride in carbon tetrachloride, and the concentration of the intercalating agent was progressively increased by volumetric additions. Values of the electrical resistance, recorded as a function of the concentration, gave direct information about the onset of intercalation.

Pyrolytic graphite specimens containing a wide range of defect compositions have been studied. The defects were introduced by variations in the preparative method, by radiation damage, and by thermal annealing. Observed intercalation thresholds are discussed below with reference to the particular defects likely to be present in any specimen.

## EXPERIMENTAL

*Materials.*—The liquid reagents used were of AnalaR quality.

The specimens of graphite used were prepared in this laboratory by the pyrolysis of methane (cf. ref. 2). In the following, deposits used without further thermal treatment are designated " type A (nominal deposition temperature) " and annealed deposits " type AB (deposition temperature, annealing temperature)." Special deposits are further described in the text. For convenience, the materials used are listed in the Table.

Graphite deposits used in the present study.

| Sample number | Deposition temperature | Annealing temperature | Specific resistance (ohm cm. $\times 10^5$) | Remarks |
|---|---|---|---|---|
| 1 | 2150° | — | 5·5 | Stress-recrystallised at 3600° [3a] |
| 2 | 1950 | — | 31·0 | Grossly misoriented |
| 3 | 2180 | — | 19·8 } | |
| 4 | 2180 | — | 19·4 } | |
| 5 | 2180 | 3000° | 5·2 | Outer layer of type AB material |
| 6 | 2180 | 3000 | 11·0 | Unirradiated type AB material, cf. samples 9, 10, and 11 |
| 7 | 2180 | 3000 | 3·4 | Inner layer of type AB material, cf. sample 5 |
| 8 | 2180 | — | 45·5 (after irradiation) | Cut from same deposit as samples 3 and 4 |
| 9 | 2180 | 3000 | 28·0 (after irradiation) | |
| 10 | 2180 | 3000 | 11·9 (after annealing) | Annealed 650° * |
| 11 | 2180 | 3000 | 11·2 (after annealing) | Annealed 1350° |
| 12 | 1800 | — | 120 | Not illustrated, no uptake |
| 13 | 2180 | — | 16·5, 18·5 | Type A, used for successive intercalation |

* Irradiated type AB material, cf. sample 6.

It should be noted that the maximum annealing temperature of 3000°, available in the experiments described below, does not always suffice to ensure complete recrystallisation. For example, deposit 6 (see Table), after annealing, is more perfect than deposit 5 or 7.

*Apparatus and Procedure.*—Samples of graphite (*ca.* 25 × 4 × 0·5 mm.) were cut to size with a jeweller's fine saw and cleaved with the *c*-axis normal to the face. It was not necessary to polish the faces in any way. The holes for the potential probes, BB (Fig. 1), were drilled slowly with 0·016 ῾n. drills held in a pin chuck, and the debris was removed by frequent drill reversal. Carbon dust was then removed by washing in carbon tetrachloride. The tablets so prepared were mounted in an *a*-axis conductivity sample holder (Fig. 1). This was immersed in various solutions of halogens in carbon tetrachloride. To the Pyrex vessel (maintained at 18 ± 2°) containing 80 ml. of carbon tetrachloride, were added, with stirring, known volumes

of bromine or of a 50% v/v solution of bromine in carbon tetrachloride, by use of a calibrated piston pipette which delivered $1.520 \pm 0.008$ cm.³ of liquid at each stroke. After each addition of halogen, the resistance of the solid sample was measured at intervals by use of a d.c. 4-point method capable of detecting changes of resistance of *ca.* 0.3% before the onset of intercalation. The specimen was allowed to reach a new steady-state resistance before further additions were
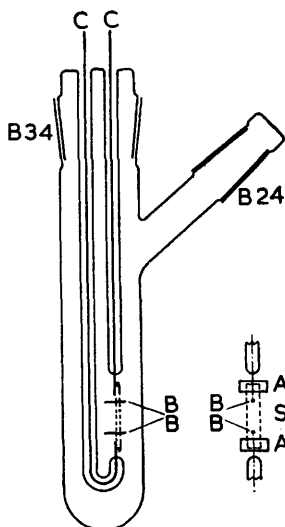


FIG. 1. The conductivity cell. The sample (S) is clamped between thin (10 thou.) platinum-foil current electrodes, AA, and the potential probes (24 S.W.G. Pt), BB, are inserted in pre-drilled holes. The two potential-probe leads are similar to the platinum current electrode leads, CC, but have been omitted for clarity.

made. With the less-perfect samples, adjustment to each new steady state took up to several days, but with the most-perfect specimen, described below, about 30 min. were required.

The mole fraction of bromine in the solution was calculated from the quantities added, but to allow for possible losses by evaporation steady-state concentrations were checked by iodometry. This check proved to be necessary only for experiments in which the number of additions was greater than ten. Values of the steady-state resistance, $R$, are recorded in the form of proportional increments $(R_0 - R)/R_0$, where $R_0$ is the resistance of the original graphite specimen.

With iodine monochloride the procedure was similar.

RESULTS

*Type A and Type AB Graphites.*—Recorded in Fig. 2 are the steady-state values of the proportional decrease in resistance plotted as a function of the mole fraction of bromine for a representative series of samples of pyrolytic graphite (see Table). For the least-perfect sample 12, type A(1800°), no decrease in resistance was observed even when the specimen was immersed in pure liquid bromine. This agrees with the finding [2] that, for graphites deposited from methane in this temperature range, bromine intercalation was immeasurably small. As shown in Fig. 2 for sample 2, type A(1950°), the relative resistance $R/R_0$, begins to decrease at a bromine mole fraction of 0.15, and continues to do so gradually with further increase of bromine mole fraction. For deposition temperatures in the region 2150—2180°, a sharper, more clearly defined threshold begins to appear; *e.g.*, both samples 3 and 4 showed thresholds near a mole fraction of 0.13. Some variability in behaviour, observed at low degrees of intercalation, is probably genuine, and may be attributed to a lack of uniformity in specimens prepared by the technique of Brown and Watt.[3a]

*Effects of Annealing.*—During deposition, the temperature drop through the sample thickness is about 350° mm.⁻¹.[3] With nominal surface deposition temperatures of about
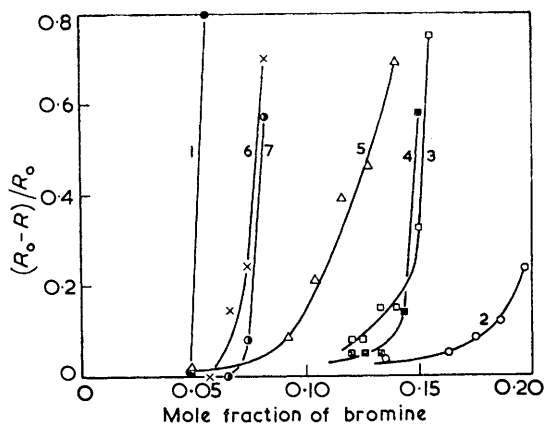
[3] Moore, Ubbelohde, and Young, *Brit. J. Appl. Phys.*, 1962, **13**, 393.
[3a] Moore, Ubbelohde, and Young, unpublished results.

2100°, as the thickness of the deposit rises appreciably above 1 mm., innermost regions reach temperatures exceeding 2450°. Above this temperature, some recrystallisation of the graphite can occur during deposition. This is manifested by stepwise improvements in $p$-factor, $a$-axis conductivity, and dispersion of the $(00l)$ X-ray reflections.[2,4] From such a deposit it is difficult to cut a truly homogeneous layer. However, it can be seen that sample 7, type AB(2180, 3000°, inner), taken from the inner layers, exhibits a sharp threshold which is similar in position and shape to that obtained with the fully-stress-relieved, homogeneous sample 6, type AB(2180, 3000°), in contrast with the markedly inhomogeneous sample 5, type AB(2180, 3000°, outer). Curve 1 represents data obtained on a special sample recrystallised under a $c$-axis compressive stress at about 3600°. This sample shows nearly single-crystal behaviour in several respects.[5]

These findings illustrate how the intercalation threshold is both sharpened and reduced as the overall perfection of the graphite is increased.



FIG. 2. The onset of intercalation of bromine for a representative series of samples, illustrating the effect of thermal history. The curves are numbered as in the Table. 1, Stress-recrystallised at 3600°. 2, A(1950°). 3, A(2180°). 4, A(2180°). 5, AB (2180, 3000°, outer). 6, AB(2180, 3000°, homogeneous). 7, AB (2180, 3000°, inner).

*Effects of Radiation Damage followed by Annealing.*—By exposure to a low degree of neutron irradiation, any defect distribution established during deposition and heat treatment can be modified in ways which can also be identified and studied by other means. Two graphites known to differ greatly in original crystallite misorientation were selected for examination after irradiation. One was part of a poorly oriented deposit, type A(2180°), 1·5 mm. thick. To allow for any lack of uniformity in this deposit, it was cleaved into three layers each measuring $25 \times 5 \times 0·5$ mm. The middle layer was then irradiated at about 20° in a hollow fuel element in the Harwell reactor BEPO to a total fast-neutron dose of $1·2 \times 10^{18}$ nvt (Ni-dosimeter). Threshold behaviour for bromine intercalation of the three layers was compared as described above. Results recorded for samples 3 and 4 (Fig. 3) show that the upper and lower unirradiated layers behave practically identically except for the variability at low degrees of intercalation, referred to above. On the other hand, the irradiated middle layer gives a curve (8) which is comparable with that for structurally more-defective graphites. After irradiation, the threshold becomes more diffuse and moves to higher concentrations.

For the second graphite, type AB(2180, 3000°), the initial crystallite misorientation was much less; it was divided into four equivalent homogeneous layers [6, 9, 10, and 11 (Fig. 4)] each 0·5 mm. thick. Three of the layers (9, 10, and 11) were irradiated at *ca.* 20° to a fast-neutron dose of $0·6 \times 10^{18}$ nvt. The threshold for the other layer (6), which was not irradiated, should be compared with those of the irradiated sample 9 and the two

[4] Blackman and Ubbelohde, *Proc. Roy. Soc.*, 1962, *A*, **266**, 20.
[5] Ubbelohde, Young, and Moore, *Nature*, 1963, **198**, 1192.

similar irradiated samples which were annealed after irradiation, 10 for 2 hr. at 650° and
11 for 2 hr. at 1350°. It may be noted that curve 9 (Fig. 4) is sharper and shows a lower
" net threshold " than does curve 8 (Fig. 3), even after allowance for the difference in dose.
Furthermore, in both Figs. 3 and 4 the irradiated specimen shows incipient intercalation
at mole fractions *lower* than for similar unirradiated graphites.

*Thresholds with Other Intercalating Agents.*—Since the primary object was to investigate
the relation between defect structures and thresholds, most of the experiments described
in this paper were carried out with reference to the intercalation of bromine. In this
connection, it is of interest to determine to what extent initiation of separation of the
carbon hexagon layers in graphite depends on the characteristics of the intercalating
molecules used. For example, other studies [1] indicated that at room temperature iodine
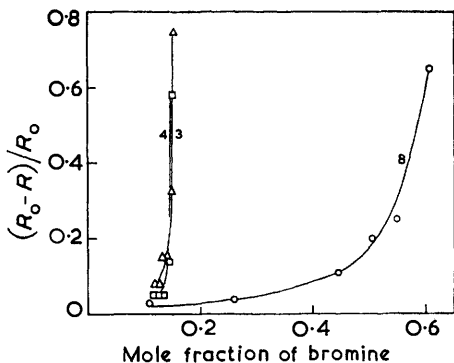


FIG. 3.

FIG. 4.

FIG. 3. The effect of fast-neutron irradiation on the onset of intercalation of bromine
by a type A(2180°) sample. The curves are numbered as in the Table. Curves 3
and 4 refer to unirradiated material and curve 8 to material which had been
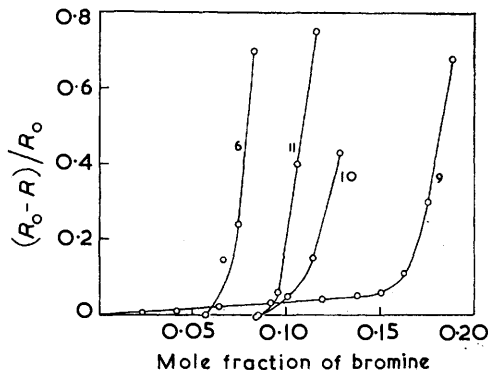irradiated to $1.2 \times 10^{18}$ nvt at 20°.

FIG. 4. The effect of fast-neutron irradiation and partial annealing on the onset of
intercalation of bromine by a type AB(2180, 3000°) sample. The curves are
numbered as in the Table. Curve 6 refers to the unirradiated material and curve
9 to irradiated material ($0.6 \times 10^{18}$ nvt) without subsequent heat treatment.
Curve 10 represents the behaviour after annealing for 2 hr. at 650° and curve 11
the behaviour after annealing for 2 hr. at 1350°.

monochloride could be intercalated into type A(2180°) graphite at mole fractions of the
order of 0.004, considerably lower than for bromine at the same temperature. In the
present investigation, iodine monochloride was used in minimal quantities to determine
its effect on the ingress of bromine present in the same solution. For this purpose, a
procedure of successive interactions was adopted.

Iodine monochloride was first added to a mole fraction of about 75% of its normal
threshold value for the particular graphite used, 13, type A(2180°). Though no bulk
intercalation of iodine monochloride could be detected from the electrical resistance,
subsequent addition of bromine to the same carbon tetrachloride solution, in a concen-
tration which of itself was less than 15% of the threshold with pure bromine, led to com-
plete intercalation of this halogen as illustrated in Fig. 5(a). Corresponding tests were
also made in the reverse order. Bromine was first added to a mole fraction of about two-
thirds of the net threshold value. No intercalation ensued at this stage. When this was
followed by additions of iodine monochloride to mole fractions up to about one-third the
normal threshold for this halogen, complete intercalation of the halogens from the mixed
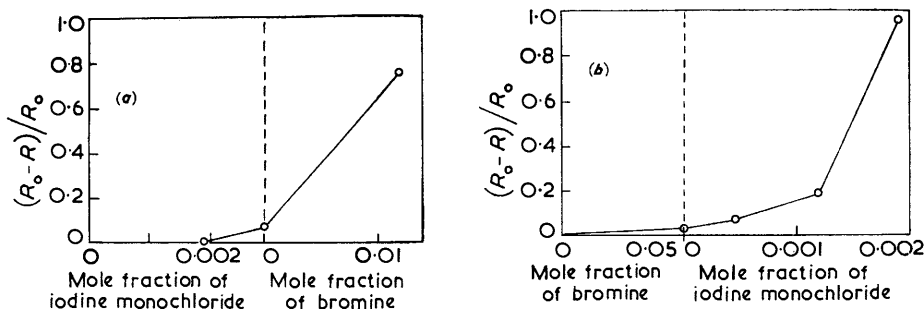solution followed [Fig. 5(b)].

FIG. 5. Successive intercalation using sample 13, type A(2180°): (a) The addition of iodine monochloride to a mole fraction of about 75% of its normal threshold value for this graphite, followed by addition of bromine to about 10% of its normal threshold value. (b) The addition of bromine to a mole fraction of about 60% of the normal threshold value, followed by successive additions of iodine monochloride up to 50% of its normal threshold value.

## DISCUSSION

As a working hypothesis, the results may be conveniently discussed in terms of sensitisation processes, probably dependent on adsorption of the halogen, followed by opening-up processes in which the carbon hexagon layers separate so as to allow inter-calation of the halogen.

A reasonable simplifying assumption is that the different graphites studied show similar adsorption properties, so that differences of threshold must depend primarily on opening-up processes. In this connection, it may be noted that physical adsorption of the halogen below the threshold is unlikely to differ greatly for the different specimens, since the methods of cutting the samples (see above) leave the edges and faces in a roughened condition.

Following the well-known concepts of adsorption, when the graphite is immersed in solutions of bromine or iodine monochloride in carbon tetrachloride, those surface sites which are capable of adsorbing the halogen will do so in the order of their adsorption potentials (differential isosteric heats). At low concentrations, the surface coverage will be directly proportional to the concentration of the intercalate solution, whereas at higher concentrations mutual interference between occupied sites, and other factors, will lead to one of the well known types of adsorption isotherm. The view under discussion is that thresholds are conditioned by a critical adsorption whose extent varies with the resistance to be overcome in opening up the layers.

Previous work [1] showed that for a given type of graphite the threshold moves to lower concentrations as the temperature is lowered; this could be correlated with an enthalpy change of 11·2 kcal. mole$^{-1}$, in agreement with the isosteric heat of adsorption of bromine on a variety of carbons, observed by other workers. It is interesting to consider in what ways a critical degree of surface coverage can operate to permit the onset of intercalation with well-aligned graphites containing different kinds of structural defects. Dispersion forces, such as are involved in physical adsorption of the additives, would hardly reduce interlayer attraction sufficiently to permit plane separation and the onset of intercalation between carbon hexagon layers. Various more forcible mechanisms of initiation of inter-calation can be envisaged. For example, halogen molecules at adsorption sites may break weak non-graphitic carbon–carbon bonds between the layers, forming strong covalent linkages between carbon and halogen. In effect, this is a form of chemisorption on the graphite. Such non-aromatic bonds at the edges of crystallites, and at other regions of extended disorder in graphite are at present difficult to characterise. A simpler alter-native involves actual electron transfer, from defect sites in the network at which the

electron density is highest, to the halogen, leaving the network positively and the halogen negatively charged. Progressive attachments of this kind on to neighbouring pairs of planes would weaken the attractive force between them, on account of electrostatic repulsions.

A semi-quantitative guide to the magnitude of the repulsive forces between planes, which can originate from negative halogen ions chemisorbed on the prism faces and from positive holes trapped at network imperfections, can be obtained by considering the principal electrostatic terms. The potential energy of interaction between negative halogen ions on successive planes, *i.e.*, nominally separated by 3·35 Å, is 4·3 ev. This therefore represents the maximum repulsive energy which can be obtained from adsorbed ions at the edges of planes, taken in pairs.

A second electrostatic contribution arises from repulsive interactions between a pair of planes each carrying $n$ trapped electronic charges per atom pair, and is of the order $fn^2e^2/r_0$, where $r_0$ if the nominal separation, and $f$ is a small numerical factor.

To ensure intercalation, this electrostatic contribution is assumed for simplicity to override the dispersion interaction at the equilibrium distance (3·35 Å), taken to be 0·7 ev per atom pair.[6] On this basis, and neglecting the contribution from repulsion terms in the chemisorbed monolayer, referred to in the previous paragraph, $n$ is found to be of the order of 0·4 trapped charges per atom pair. Although qualitative. these estimates are informative because they suggest that intercalation will not be propagated through the crystal planes until charge transfer approaching the stoicheiometric level has occurred. Much more detailed studies of intercalation kinetics are required to explore this suggestion further. Increasing separation of the planes at the edges, due to coulombic repulsion within the adsorbed monolayer, seems likely to facilitate further electron transfer from these networks, since our present experimental evidence suggests that once an interplanar layer begins to be stocked in this way, the process goes to completion before the next layer is begun.[1] On this particular model for initiation of intercalation, the critical quantity to be exceeded before intercalation proceeds refers primarily to the extent of charge transfer. On this view, the greater effectiveness of iodine monochloride compared with bromine can be attributed to its permanent dipole moment and greater electronegativity.

The fact that the mean diameter of the iodine-monochloride molecule is considerably larger than that of bromine (2·67 compared with 2·28 Å) provides some evidence against an alternative possibility, namely that onset of intercalation requires that the intercalating agents must diffuse through interplanar space to sites of pinning defects, in order to unpin the layers internally by chemisorption. For more highly defective graphites, the role of pinning at internal defects in a crystallite cannot however be excluded as contributing to the threshold.

*The Influence of Crystal Defects on Intercalation Thresholds.*—Whilst it is clear that the simple electrostatic model outlined above can represent the act of separation of the carbon hexagon planes at some early stage, more detailed hypotheses are necessary to explain why thresholds are different in value and type for different graphites.

For recrystallised pyrolytic graphite in which the individual crystallites are not themselves ideal, the fact that the crystallite under consideration is embedded in a matrix of other crystallites, which are differently oriented and have different intrinsic thresholds, may displace its threshold to lower or higher values according to whether the net strain in the *c*-axis direction of the crystallite is tensile or compressive. In highly oriented samples, intercalation occurring in surface crystallites, located in the prism faces, should facilitate intercalation in crystals located in the interior, though no progressive enhancement of threshold values should be observed for intercalation in this case. Within the crystallites, the relative orientation of adjacent hexagon-layer planes and the interactions

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[6] Ubbelohde and Lewis, " Graphite and its Crystal Compounds," Oxford University Press, London, 1960.

between basal-plane dislocations and vacancy clusters in adjacent planes must somewhat affect the interplanar bonding energies. Stacking disorder, leading as it does to a larger interplanar distance, will presumably decrease the bonding energy whereas long, relatively weak, homopolar bonds between the unsatisfied trigonal hybrids at vacancy clusters will increase the bonding energy. Another origin of gradual thresholds would appear to be the presence of interstitial atoms between the hexagon planes. By leading to local dilatation in the hexagon networks, these must produce local increases and reductions in interplanar distance at different parts of the crystallite and thus generate a spectrum of intrinsic thresholds.

Brief comment may be made about effects of deposition temperature and of reactor irradiation in the light of these considerations.

In samples (type A) deposited at the lower temperatures, crystallites are somewhat smaller than in annealed material (type AB). However, the main difference between the two groups of graphites arises from the suppression, by annealing, of regions of more extreme misorientation of the basal-plane directions. This would appear to account for the differences recorded in Figs. 2 and 3 between unirradiated type A and type AB graphites.

Neutron irradiation, with the low doses used in this work, should produce interstitial clusters and individual vacancies. This type of radiation damage can affect the intrinsic threshold, but should not introduce new crystallite misorientation. In poorly oriented material, results (Figs. 3 and 4) suggest that radiation damage raises the intrinsic threshold for some crystallites and decreases it for others. On intercalation it is to be expected that those interplanar spaces which can most easily be attacked will be filled first. As a consequence, $c$-axis compressive stresses will be exerted on the remaining crystallites, thus raising their intrinsic threshold and giving rise to a gradual intercalation curve. This effect is larger in type A than in type AB graphites.

Thus in graphite with better initial orientation of crystallites (Fig. 4), irradiation displaces the threshold to higher mole fractions, with a low-energy tail, but does not introduce a broad spectrum of thresholds comparable with that observed for the specimen in Fig. 3. It is known from other work that on annealing to 650°, the interstitial clusters in well-oriented graphite are removed; however, vacancies are hardly affected, though some clustering of these might have occurred. With graphite in this condition the intercalation threshold is lowered but is still somewhat diffuse (Fig. 4). After annealing to 1350°, the vacancies aggregate into basal-plane dislocation loops with the Burgers vector normal to the basal plane. Fig. 4 shows that this leaves the threshold unaltered, but the sharper form of the curve points to a secondary influence from the change in distribution of the vacancies in the networks. Until threshold determinations can be made for perfectly aligned defect-free crystals, attribution of these effects to the various factors considered above must be regarded as tentative. In the meantime, the physicochemical method described would appear to provide a useful tool for diagnosing isolated and co-operative defects in well-aligned and near-ideal graphites.

The results on the modification by one halogen of intercalation of another point to the use of catalytic methods in forming new crystal compounds of graphite.

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