39. *Some Physical Properties Associated with " Aromatic " Electrons. Part III. The Pseudo-metallic Properties of Potassium–Graphite and Graphite–Bromine.*

By F. R. M. McDonnell, R. C. Pink, and A. R. Ubbelohde.

Graphite is known to form " lamellar compounds " C_8K and C_8Br by absorption of potassium and bromine, respectively. Physical properties of these compounds have been studied to elucidate the nature of the bonding, and its effects on the aromatic π electrons in graphite.

The marked diamagnetism associated with the π electrons in graphite is destroyed in both compounds. C_8Br is weakly diamagnetic, and C_8K shows a temperature-independent paramagnetism of the same order as for metallic calcium. Both compounds are better conductors of electricity than is graphite.

A tentative interpretation of these effects is given in the light of the band theory of the energy levels in graphite. The layers of fused aromatic nuclei are regarded as amphoteric, and can both take up electrons from the potassium atoms, and give them up to the bromine atoms, yielding pseudo-metallic structures in both cases.

Magnetic and electrical data on a compound of formula C_4F whose structure has not yet been established by other means suggest a general similarity in behaviour with graphite.

In Parts I and II (Pink and Ubbelohde, *Trans. Faraday Soc.*, 1948, **44**, 708; McDonnell, Pink, and Ubbelohde, *ibid.*, 1950, **46**, 156), the possibility of resonance coupling of " aromatic " electrons in *cyclo*octatetraene was studied by means of the magnetic susceptibility and its temperature coefficient. With graphite, in addition to the magnetic susceptibility, other physical properties such as the electrical conductance can give important information about the π electrons. The present investigation was carried out to determine how far these electrons are affected by the formation of " lamellar compounds " in which foreign atoms or groups are intercalated between the layers of fused aromatic nuclei. For reasons of simplicity, the " compounds " C_8K and C_8Br were studied in the first instance. A substance of unknown structure with the empirical formula C_4F which was made available by Imperial Chemical Industries Limited was included, since it seemed likely to show related behaviour.

As is detailed below, the main result of these investigations is to show that the π electrons are very markedly affected by the intercalated atoms. The behaviour of both C_8K and C_8Br is actually closer to that of " good " metals than that the parent graphite. The properties of C_4F suggest a different mode of binding of fluorine from the binding of potassium or bromine with the graphite.

EXPERIMENTAL.

Graphite was available in a wide variety of samples, both polycrystalline and in the form of crystals of 1 mm. or more edge, from natural sources, and from " Kish," kindly supplied by B.I.S.R.A. However, work on single crystals did not seem profitable owing to the break-up which takes place on forming the lamellar compounds. The bulk of the work was therefore carried out on a sample of polycrystalline graphite specially freed from paramagnetic ions, and of high purity, kindly supplied by A.E.R.E. Its analysis showed :

Ash, 0·09%. Specific impurities, in p.p.m. : Ca 300, Va 130, Si 130, Fe 40, Ti 25. Less than 5 p.p.m. : B, Cd, Li, Mg, Mn, Pb, Sn, W, Mo, Ni, Bi, Be, Co, Ag, Zn, Sb, As, Cr, Al, Ba, Sr, In, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu.

Inspection of Debye–Scherrer *X*-ray diagrams with stationary specimens showed that the crystallites gave reflections with (*hki*0) sharp, (000*l*) rather diffuse, and (*hkil*) with *l* large, very diffuse. Thus the lamellar spacings appear to be well defined. The extension of the layers and the accuracy of orientation about the *c* axis do not extend beyond about 10^{-5} cm.

Samples of graphite used for susceptibility measurements were degassed *in vacuo* for 2 hours at 500° before being transferred *in vacuo* to a previously calibrated Gouy tube.

Potassium–Graphite.—Potassium metal (B.D.H.) was used as a starting material. Before use it was filtered from oxide and distilled twice in a Pyrex vessel. These distillations were conducted at a low temperature to prevent the formation of the paramagnetic yellow peroxide KO_2 (Neuman, *J. Chem. Physics*, 1934, **2**, 31). The final material was shown by measurements at different field strengths to be free from ferro-magnetic impurites; m. p. (cooling curve) 63·4° (I.C.T. give 62·3°).

Potassium–graphite was prepared by the method of Fredenhagen and Suck (*Z. anorg. Chem.*, 1929, **178**, 353), which ensures that contact between the potassium and the graphite occurs only through the vapour phase. In the early experiments the major difficulty encountered in this preparation was the formation of a brown substance, probably KO_2, resulting from the attack of potassium on the Pyrex walls of the vessel during the prolonged periods of heating required. The quantity of this substance formed was sufficient in some instances to cause flakes of it to peel off the walls of the apparatus. Since the possibility of the admixture of KO_2 with the potassium–graphite could not be tolerated, in view of its highly paramagnetic nature, the whole of the apparatus was finally constructed from a special glass resistant to alkali metals, supplied by the General Electric Company, Limited. This glass (specification X4/NA/10), showed only very slight discoloration after 24 hours' exposure to potassium vapour at 400°. The potassium–graphite was transferred *in vacuo* to a previously calibrated Gouy tube, which was then sealed off.

The composition of the samples was determined from a knowledge of (i) the initial weight of graphite, (ii) the weight of potassium–graphite plus the ampoule in which it was first sealed off, and (iii) the weight of the ampoule determined subsequently by weighing it empty after transfer of the contents to the Gouy tube, together with the collected fragments of glass. The composition of different samples varied within the limits $KC_{8\cdot47-7\cdot79}$. The potassium-rich specimens may have contained some free potassium. Special precautions were used to carry out all measurements on potassium–graphite in high vacuum, since this compound rapidly autoxidises in air and since KO_2 is paramagnetic.

Preparation of Graphite–Bromine.—Graphite–bromine was prepared by keeping graphite over bromine in a sealed vessel for 24 hours (Thiele, *Z. anorg. Chem.*, 1932, **207**, 340; Rudorff, *ibid.*, 1941, **245**, 383). It was then quickly transferred to another vessel, which was cooled in liquid air, evacuated for some time, and then transferred to ampoules for sealing-off or to a previously calibrated Gouy tube as required. In this process some bromine was invariably lost. The actual composition of the samples of graphite–bromine on which measurements were made was determined as in the case of C_8K from a knowledge of (i) the weight of graphite, (ii) the weight of graphite–bromine plus ampoule, and (iii) the weight of the recovered ampoule.

" AnalaR " Bromine was used without further purification in the preparation of graphite–bromine. Its susceptibility was $-0{\cdot}337 \times 10^{-6}$ as compared with reported value of $-0{\cdot}39 \times 10^{-6}$ (I.C.T.).

The " tetracarbon fluoride " contained a ferromagnetic impurity, probably Fe_2O_3, which was removed by extraction (Soxhlet) with hot concentrated hydrochloric acid for 4 hours, after which it was washed free from chloride and dried. Even after this treatment it retained a temperature-dependent paramagnetism probably due to impurity (cf. Table I).

Bulk Densities.—For purposes of comparison with other data, the bulk densities of the various compounds were determined in the different conditions used for the resistivity and magnetic measurements. The data are recorded in Tables I and II.

Magnetic Measurements.—Susceptibility measurements were made by the Gouy method in the apparatus already described (McDonnell, Pink and Ubbelohde, *loc. cit.*). The only new feature was the use of a calibrated resistance and a microvolt potentiometer to measure the current through the magnet coils more acccurately (to ±0·02%) than could be done with a calibrated ammeter. For the determination

TABLE I.

Magnetic susceptibilities (c.g.s. × 10^{-6}).

	90° K. :		195° K. :		288° K. :		Bulk density in Gouy tube,
Substance.	χ_s.	χ_m.†	χ_s.	χ_m.†	χ_s.	χ_m.†	g./c.c.
Potassium	+0·540	+21·1	+0·538	+21·0	+0·539	+21·1	0·849
Graphite (A.E.R.E.)	−7·909	−94·81	−6·757	−81·08	−6·04	−72·48	0·783
$KC_{8\cdot47}$	+1·01	+16·78	+1·01	+16·78	+1·00	+16·61	0·730
$KC_{7\cdot79}$	+0·953	+16·23	+0·951	+16·17	+0·953	+16·23	0·713
$BrC_{9\cdot98}$	−0·411	−8·23	−0·399	−7·99	−0·403	−8·07	0·979
C_4F *	−0·503	−8·43	−0·523	−8·76	−0·527	−8·83	0·860
	−0·538	−9·03	−0·539	−9·05	−0·538	−9·03	
Bromine	—	—	—	—	−0·337	−26·96	3·13

* C_4F contained a temperature-dependent paramagnetic component (see above). The lower set of data has been corrected on the assumption that the paramagnetism is due to an impurity obeying the Weiss–Curie law.

† For graphite and its compounds χ_m has been calculated per g.-atom of carbon, to permit ready illustration of any effect on the electrons.

FIG. 1.

Apparatus for measurement of resistance of various lengths of compressed graphite and its compounds.

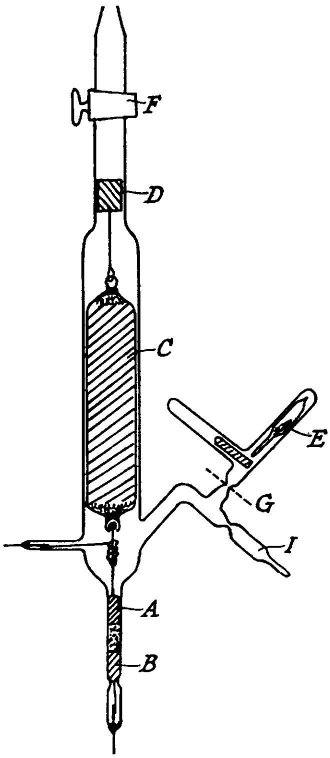
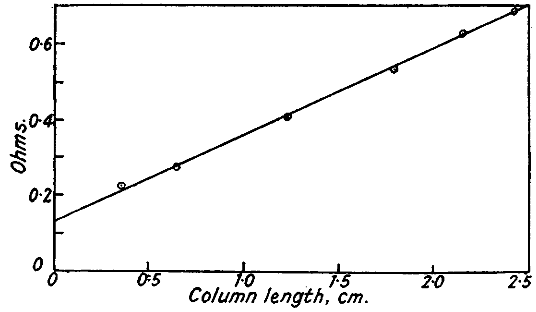


FIG. 2.

Resistance of columns of compressed graphite.



of the temperature coefficients of susceptibility measurements were in each case made at 90° K., 195° K., and 288° K. The Gouy tubes were calibrated with boiled-out distilled water, the specific susceptibility of which was taken to be −0·720 × 10^{-6} c.g.s. units. Field strengths used were approximately 3700 and 2100 gauss. Except where otherwise stated, susceptibilities were found to be independent of field strength. Magnetic data are recorded in Table I.

Electrical Conductance and Thermoelectric Measurements.—The conductances were measured in the apparatus shown in Fig. 1, which permitted measurements to be made at a constant compression of 20·3 kg./cm.² in a high vacuum. The two electrodes *A* and *B* are of brass; *B* is a close-sliding fit in the glass tubing and is held firmly in position with picein wax; *A* is a loose-sliding fit. Connection is made to the bridge through the two tungsten seals. The lead weight *C* for compression of the powdered solids is encased in glass and has a mass of ~2 kg. *D* is a piece of soft iron which allows the upper electrode *A* to be held outside the electrode chamber magnetically while the substance under investigation is being added. The sample whose conductance is to be measured is contained originally in a sealed ampoule in *E*. When the apparatus has been evacuated, *F* is closed, the tip of the ampoule is broken off by allowing the weight to drop on the ampoule tip, and the sample shaken into the chamber *I*. A seal is then made at *G*. The substance is finally transferred to the electrode chamber in portions, a series of resistance measurements being made for columns of powder of heights ranging between 0·2 and 3·0 cm. Column heights were measured to ±0·002 cm. with a travelling microscope. Corrections for leads and contact resistances were obviated by calculating the specific conductance from a knowledge of the cross-sectional area of the electrode chamber (0·118 sq. cm.), and the gradient of the plot of resistance against length of column. The data for graphite are shown in Fig. 2. The extrapolated curve does not pass through the origin, owing to the contact resistances at the brass electrodes. Conductance data calculated in this way are shown in Table II.

The same apparatus without modification was used for measurement of the thermoelectric E.M.F.'s. In these measurements a 3-cm. column of powdered solid was used, of which 1 cm. was immersed in liquid air. Owing to the short length of column which had to be used, it is unlikely that the hot junction fully attained the room temperature, but the signs and magnitudes of the effects recorded in Table III are comparative.

TABLE II.

Conductances of graphite and its compounds.

Substance.	Bulk density, g./c.c.	Conductance (ohm^{-1} cm.$^{-1}$). 90° K.	288° K.	Substance.	Bulk density, g./c.c.	Conductance (ohm^{-1} cm.$^{-1}$). 90° K.	288° K.
Kish	1·90	110	128	C_4F after heating *in vacuo* for 12 hrs. at 500°	0·968	—	17·0
Graphite (A.E.R.E.)	1·19	26·5	35·2	$BrC_{10\cdot5}$	1·41	—	223
$KC_{8\cdot47}$	—	—	1462	$BrC_{9\cdot9}$	1·92	197	384
$KC_{8\cdot46}$	—	1302	980	Metallic K (compact)	0·86	—	150,000
$KC_{8\cdot46}$	1·40	—	1271	Powdered Cu	2·15	—	850
$KC_{12\cdot2}$	—	1073	870	Compact Cu	8·3—8·9	—	580,000
$KC_{27\cdot8}$	1·05	—	565				
C_4F	1·03	0·222	0·389				

Note: The crystal density of graphite is 2·26 g./c.c. (Hoffmann, Wilm and Caslan, *Z. Elektrochem.*, 1936, **42**, 504).

TABLE III.

Thermo-electric voltage of graphite and its compounds against brass.

Substance.	E.M.F. (mv.) against brass, showing sign of hot junction.	Substance.	E.M.F. (mv.) against brass, showing sign of hot junction.
Kish	−0·5	$BrC_{9\cdot9}$ *	−2·4
Graphite (A.E.R.E.)	−1·4	C_4F	−1·5
$KC_{8\cdot47}$	+2·0	C_4F after heating for 12 hrs. *in vacuo* at 500°	−2·5
$KC_{12\cdot2}$	+2·2		
$KC_{27\cdot8}$	+2·4		

* Thin platinum foil over the brass electrodes.

In all the measurements with graphite–bromine the tips of the brass electrodes were protected with thin platinum foil.

DISCUSSION.

The broad general conclusion which emerges from the examination of the data in Table I—III is that graphite actually becomes " more metallic " on forming C_8K or C_8Br. The marked diamagnetism associated with the giant π orbitals is destroyed, and the electrical conductance is increased. These observations can be tentatively interpreted on the basis of a model in which the layers of graphite behave amphoterically, and take up electrons from the potassium, or give up electrons to the bromine. The bonds between the K or Br atoms and the graphite layers are probably " metallic " in nature. As in other inter-metallic compounds a range of compositions around the stoicheiometric value has approximately the same stability. Various aspects of this suggestion may be examined as follows.

(i) *Bond distances and bond energies of the lamellar compounds. X*-Ray-diffraction measurements show that the interlamellar distance of 3·35 A. in graphite increases to 7·76 A. when potassium forms C_8K and to 7·05 A. when bromine forms C_8Br (Schleede and Wellman, *Z. physikal. Chem.*, 1932, **18**, *B*, 1; Rudorff, *loc. cit.*). If the ions K^+ (radius 1·33 A.) and Br^- (radius 1·95 A.), respectively, were packed into layer ionic lattices, with the amphoteric layers of carbon atoms carrying charges of opposite sign, this should give the smaller spacing for the potassium layer lattice, contrary to what is observed. But if the potassium and bromine atoms form essentially pseudo-metallic linkages with the layers of carbon atoms, the larger spacing required by potassium (metallic radius 2·23 A.) than by bromine (covalent singly-bonded radius 1·19 A.) is less difficult to understand.

The absorption of bromine as molecules (one of the hypotheses quoted by Rudorff, *loc. cit.*) does not explain the smaller space requirements compared with the potassium compound. [When our experiments were completed Goldsmith (*J. Chem. Physics*, 1950, **18**, 523) published magnetic studies on graphite–bromine on the basis of which he also postulated mainly intercalated bromine molecules.] Magnetic properties are further discussed below. A further objection to the assumption of absorbed bromine molecules is that this does not explain the effect of bromine on the conductance, and the concurrence in behaviour between bromine and potassium.

Complete energy data for the formation of the compounds are not available, but some data are available (Bichowsky and Rossini, " Thermochemistry of Chemical Substances," Reinhold, 1936, except where otherwise stated).

$$K_{gas} \longrightarrow K^+_{gas} + e;\ \Delta H_1 = +101{\cdot}1 \text{ kcals. mole}^{-1} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

These electrons fill the empty band in graphite (Wallace, *Physical Rev.*, 1947, **71**, 622; Coulson, *Nature*, 1947, **159**, 265) starting from a zero ground level which may conveniently be written as

$$e + [C_{lam.}] \longrightarrow [C^-_{lam.}];\ \text{(approx. thermoneutral)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The K⁺ ions are then intercalated by virtue of the electrostatic charges on the lamallæ :

$$K^+_{gas} + [C^-_{lam.}] \longrightarrow C_8K + \Delta H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Addition of (1), (2), and (3) gives for the overall process

$$K_{gas} + [C_{lam.}] \longrightarrow C_8K;\ \Delta H = \Delta H_2 + 101{\cdot}1$$

From the data of Fredenhagen and Cadenbach (*Z. anorg. Chem.*, 1926, **158**, 249)

$$K_{liq.} + [C_{lam.}] \longrightarrow C_4K_{(excess\ K)};\ \Delta H = -6{\cdot}0$$

If the value for C_8K is taken to be of the same order, this would make

$$K_{liq.} + [C_{lam.}] \longrightarrow C_8K;\ \Delta H = -6{\cdot}0$$

or

$$K_{gas} + [C_{lam.}] \longrightarrow C_8K;\ \Delta H = -25{\cdot}2$$

so that $\Delta H_2 \approx -126$ kcals./mole.

This large energy evolution compensates for the ionisation energy of the potassium. Absorption of vapour proceeds readily when the vapour pressure of the potassium is ~0·005 atm. It is noteworthy that for sodium, where the ionisation energy is larger ($\Delta H_1 = +119{\cdot}5$ kcals./mole), the energy evolved on intercalation of Na appears to be insufficient to compensate the higher ionisation energy, since no lamellar compounds of graphite and sodium are known, whereas rubidium and cæsium, which have lower ionisation energies than potassium, both form lamellar compounds (Riley, *Fuel in Science and Practice*, 1945, **24**, 1). The non-intercalation of other metal atoms such as cadmium can probably be explained on similar lines.

For the bromine compound the net energy requirement of the process

$$\tfrac{1}{2}Br_{2\ gas} + e \longrightarrow Br^-_{gas};\ \Delta H_1 = -54 \text{ kcals. mole}^{-1} \quad . \quad . \quad . \quad . \quad (4)$$

strongly favours intercalation of the Br in the process

$$Br^-_{gas} + [C^+_{lam.}] \longrightarrow C_8Br;\ \Delta H_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

ΔH_3 might be expected to be lower than ΔH_2 owing to the larger size of Br^- than of K^+, but since the ultimate lamellar compounds probably involve inter-metallic rather than ionic bonds the calculation will not be pursued further. It need only be said that known energy data accord very reasonably with the pseudo-metallic model for potassium–graphite and graphite–bromine.

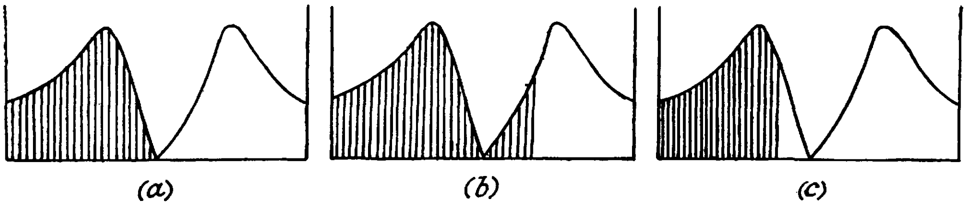
The ready wetting of C_8K or C_4K by excess of potassium (Fredenhagen and Cadenbach, *loc. cit.*, and present observations) indicates metallic bonding at the surface of separation of these two phases (cf. Ubbelohde, *J.*, 1950, 1143) and supports the general interpretation of metallic binding in these lamellar compounds.

The correspondence between the bromine and the potassium compounds though not complete is not unexpected, on the above basis, though further energy data are clearly required to complete the interpretation.

(ii) *Electrical conductivity of the compounds.* Experiments on single crystals of graphite indicate that $\sigma\perp$ is only a small fraction of the order of 10^{-4} of $\sigma =$, where $\sigma\perp$ is the conductance in a direction perpendicular and $\sigma =$ that parallel to the lamellæ. Unfortunately, the swelling and crumbling of single crystals when the lamellar compounds are formed necessitates the use of polycrystalline powders and precludes verification of whether the conductivity is equally affected in both directions by forming the lamellar compounds. A further difficulty arises with the polycrystalline powder in the interpretation of the changed sign of the temperature coefficient of conductance on compound formation. Polycrystalline graphite has a positive temperature coefficient of conductance, as has also " tetracarbon fluoride " and graphite–bromine; but C_8K has the negative temperature coefficient of conductance corresponding with a metal.

According to Wallace (*loc. cit.*), $\sigma =$ should have a negative temperature coefficient for a single crystal, and the positive temperature coefficient of polycrystalline graphite arises from the effect of temperature on the resistance *between* crystallites. However this may be, the marked increase in conductance observed in our experiments does seem to be most readily interpreted in terms of the part-filling of the empty electron band, in C_8K, and the part-emptying of the full electron band in C_8Br as sketched in Fig. 3. When the bromine or potassium is removed, the conductance falls again, so that the effects recorded in Table II can hardly be due to the influence of bromine or potassium on the " impurity atoms " at the edges of crystallites.

FIG. 3.



a. Electron energy levels in graphite according to Coulson (loc. cit.).
b. Suggested electron bands in potassium–graphite.
c. Suggested electron bands in graphite–bromine.
(*All at* 0° K.)

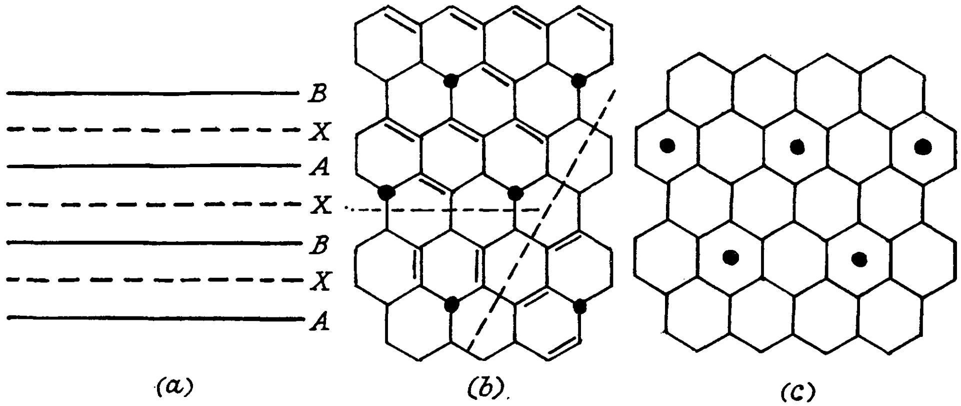
From the bulk densities, the carbon content per c.c. in the conductance experiments can be calculated as: in graphite, 0·099; in $KC_{8\cdot46}$, 0·084; in $KC_{22\cdot8}$, 0·079; in $BrC_{9\cdot9}$, 0·092 g.-atom. The increase in conductance on formation of graphite–bromine or potassium–graphite is clearly not due to a closer packing of the crystallites in the compressed powders. It is noteworthy that the conductance of powdered Cu (Table II) is of the same order as for potassium–graphite.

The change in colour in C_8K, which is a fine brown, and in C_8Br, which is steel-blue, likewise indicates that the effect of potassium or bromine is primarily on the energy levels of electrons within each crystallite. On the pseudo-metallic model suggested above for these compounds $\sigma\perp$ should show considerable increase on compound formation, but it has not yet been possible to test this. The change in magnitude and sign of the thermoelectric power against brass on compound formation gives further support to the above interpretation, since both compounds should resemble " better " metals, *i.e.*, with less completely filled energy levels than graphite.

(iii) *Magnetic data.* At present perhaps the most complete evidence about the bonding in these compounds is obtainable from the magnetic data, since here the problem of the contribution of inter-crystallite electron transitions does not arise. The weak temperature-independent diamagnetism of C_8Br is comparable with that of metals such as tin or zirconium and the comparatively strong temperature-independent paramagnetism of C_8K is comparable with that of metallic calcium. Both these are consistent with the picture obtained from the conductivity and thermoelectric data. It is noteworthy that compound formation leads to a pseudo-metal C_8K considerably more paramagnetic than pure solid potassium itself. That the electrons of the potassium must be used in bonding may be confirmed from the fact that isolated potassium atoms with unperturbed electron orbits would give a temperature-dependent magnetism which in C_8K would give χ_s $+27\cdot0 \times 10^{-6}$ at 90° K. and χ_s $+8\cdot4 \times 10^{-6}$ at 288° K., *i.e.*, much larger than, and with quite a different temperature coefficient from, the observed values. A possible dependence of the susceptibility on field strength in the sense required by ferromagnetism was observed for C_8K. So far as observed it does not exceed 1% and is under further investigation.

(iv) *Structural relationships of the atoms in* C_8K *and* C_8Br. C_8K has been subjected to *X*-ray powder analysis (see refs. by Riley, *loc. cit.*). Though the interpretation is not unique, a plausible structure appears to be as indicated in Fig. 4. [The structure of C_8Br (Rudorff, *loc. cit.*) though probably related to C_8K is doubtful and is not reproduced here.]

FIG. 4.



a. Layer-plane sequence in potassium–graphite : carbon layers, full line ; potassium layers, broken line.
b. Position of carbon layer plane A with respect to potassium ion in X, showing three possible Kekulé-bond arrangements.
c. Position of carbon layer plane B with respect to potassium ions in X.

In the preceding sections an interpretation was developed according to which the intercalated potassium and bromine atoms form metallic bonds by releasing or taking electrons from the graphite. According to an alternative description a metallic system consists of covalent bonded atoms in electron-defect resonance. With this formulation K–C bonds might be illustrated as in Fig. 4, *a*—*c*. For a given location of potassium atoms three Kekulé-bond arrangements can be described. Each of these " canonical structures " leaves one electron per potassium atom with unpaired spin. At this stage the bond model does not appear to warrant further elaboration. It does, however, give a ready explanation of the ordered arrangement of potassium (and probably bromine) in the layers, since these atoms assume definite bonding locations in the pseudo-metallic system in resonance. Less favourable Kekulé resonance structures would be formed if a disordered arrangement of the intercalated atoms were taken up.

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