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SVMMARIVM — Complura graphitis composita ostendunt optimam metallicam conductionem iuxta axem *a*; ex hoc confirmatum est posse metalla synthetica inter aromatica organica composita quaeri.

Natural metals:

More than half of the elements of the periodic system are solids with metallic conduction at ordinary temperatures and pressures. In crystal chemistry, the significance of this distinctive property was not fully understood till the development of the band theory of electron energy levels in solids. Band theory is a branch of physics which permits a fairly sharp classification of solids into metallic conductors, which contain at least one electron band only partly filled, semiconductors which have an empty electron band lying fairly close to the topmost filled bands, so that the excitation parameter ε/k is not too far from ambient temperature, and per-

mits excitation of an appreciable number of charge carriers $n = A\exp - \varepsilon/kT$ into it, and insulators in which the nearest empty band lies so high above the topmost full band, that thermal excitation of charge carriers into it can be neglected. Valence theory gives a somewhat different more chemical account of metallic properties. As discussed by PAULING and others, the resonance theory of metallic bonding involves delocalised electrons, which account for charge wandering under minimal applied voltage gradients. These delocalised electrons arise from incomplete valence shells; part of the bonding between atoms involves resonance charge switching.

Synthetic Metals:

Neither approach throws very precise light on the prospects for making synthetic metallic conductors from atoms whose compounds are normally insulators, or at best semi-conductors. However, even the most primitive form of band theory points to the fact that semi-conductors with empty bands extremely close to the topmost full band might have the characteristic excitation temperature ε/k so close to ambient, as to be practically metallic. It says nothing about the kinds of crystals to be expected. On the other hand, resonance theory suggests that chains or networks of conjugated atoms, particularly in organic compounds, involve *delocalised electrons* and could possibly lead to metallic conduction in solids that contain them. Curiously, very little attention has been paid to crystals (other than natural metals) which might show metallic conduction of electricity.

Both these approaches to metallic conduction indicate that *aromatic organic chemistry* should be a fruitful exploration ground for making synthetic metals. Organic chemists are however mostly specialists who have very little interest in the solid state. Recently, interests in certain conjugated large molecules have begun to ferment, but no great success

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has yet been reached in achieving synthetic metals by organic preparative means. On the other hand, it has been known since 1924 that crystalline graphite contains planar networks of carbon hexagon bonds. These hexagon networks were shown to be virtually identical with smaller aromatic molecules in 1933 (Ref. 1), and must thus be regarded as giant aromatic molecules. In 1947, COULSON and WALLACE (Ref. 2) produced the first realistic electron band structure for graphite. Notably this consists of an empty electron band with zero separation from the topmost full band. From either approach, Graphite thus has a number of promising characteristics for preparing synthetic metals in great variety. Combination of these scientific ideas permitted me to make the first step forward, in 1950 (Ref. 3). I had the idea of modifying the concentration of electrons in graphite, by causing it to form *charge transfer compounds*. Crystalline Graphite forms what are often described as intercalation compounds with a considerable variety of molecules. Intercalation takes place quite readily both with molecules whose general character is electron accepting, such as iodine monochloride, or bromine, and with molecules whose characteristic is strongly electron donating, including alkali metal atoms like potassium, rubidium or caesium. My hypothesis about charge transfer led to the conclusion that intercalation with (say) bromine should effectively extract electrons from the full band, whereas intercalation with (say) potassium should inject electrons into the empty band. Either process would markedly increase the number of charge carriers per unit volume, and should in consequence make the solid a much better metallic conductor.

This hypothesis was beautifully verified experimentally. It is sufficient, for example, to blow the vapour of bromine or iodine monochloride over a piece of solid graphite, to reduce its resistance by a factor of between thirty and forty. All charge transfer compounds of graphite yet prepared are much better metals than the parent graphite. A more subtle conclu-

sion also required by my hypothesis about the consequences of charge transfer was that molecular compound formation with electron acceptors must increase the number of positive holes charge carriers, producing good p – metals, whereas electron donors increase the number of negative charge carriers, producing good n-metals. This too was fully confirmed, by measurements of thermo-electric power and from the opposite signs of the Hall effect for the two types of intercalate.

I should add that this first breakthrough into the *field of synthetic metals based on graphite* was matched by numerous studies of effects of charge transfer compound formation, on the semi-conductor properties of smaller aromatic molecules. These too confirmed the general hypothesis about an increase in the number of charge carriers. With semi conductors these charge transfer compounds still demand thermal excitation energies, but often such energies are very low.

Well oriented graphite:

Though these early results were highly interesting and suggestive in a number of areas of chemical physics, they made one physical characteristic about graphite painfully evident. I refer to the extremely high anisotropy of many of its physical properties parallel or perpendicular to the carbon hexagon planes. This anisotropy had been measured, but only for properties such as thermal expansion or diamagnetic susceptibility or electrical resistivity which require only small perfect crystals to give valid measurements. What we needed was large pieces of perfect graphite to determine the anisotropy of many other physical properties. Furthermore, when one prepares intercalation compounds of graphite, insertion of the molecules causing charge transfer hardly alters the size of the carbon hexagon networks, but greatly increases the distance between them. Quite large swelling pressures operate in individual crystallites, as a consequence of this intercalation.

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For example, we have measured pressure of the order of 300 atm with graphite/bromine. As a consequence, if one starts to make large pieces of synthetic metals, starting with a block of commercial polycrystalline graphite, these crack and crumble before full intercalation can be completed.

A search through diverse hopeful geological deposits convinced us that perfect graphite in fairly large pieces was even rarer than perfect diamond of the same size, though no ladies would be interested to hang pieces of perfect graphite round their necks, as jewelry.

Accordingly, to make real progress with synthetic metals based on graphite we had to solve the technological problem of first making large pieces of well oriented graphite.

Production:

A number of only partly successful methods were tried before our present practice, which is to start with large pieces of pyrolytic graphite, and iron out textural and lattice defects by applying moderate shear stresses, whilst the material is heated above about 3000°C. "Stress-annealed graphite" as we have named the product has highly perfect distribution of its c-axes, but (for reasons I need not develop here) the crystallites though accurately parallel have their a-axes largely random. For many electronic and other physical measurements this is not however a serious objection. In particular we have already prepared quite a large variety of synthetic metals from it.

Smooth formation of crystal compounds:

As a starting material, stress annealed graphite has important advantages over any previously studied variety, for preparing very dilute as well as fully intercalated metals.

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One advantage is that the expansion which occurs as each layer becomes filled, and which takes place in the direction of the c-axis, is accurately parallel in neighbouring crystallites. It can thus take place smoothly with little or no mechanical constraint from the neighbouring crystallites in a block of well oriented graphite. In consequence, various molecules enter the layers, at much lower critical vapour pressures than in any other preparations of compounds of graphite. Furthermore, uniform intercalation can readily be controlled right up to vapour pressure at which every layer is filled. This means that *graded families of synthetic metals can now be obtained,* such as Cn Br; Cn ICl; Cn^+ $AlCl_4^-$ $AlCl_3$; Cn^+ HSO_4^-. $2H_2SO_4$; Cn^+ NO_3^-. $3HNO_3$ etc. etc. in which n can have extremely high values, in the most dilute intercalates, and has a value corresponding with complete filling of each successive layer between the carbon hexagon sheets, in the upper limit of any family of synthetic metals. Evidence which I need not detail here indicates that as soon as any crystal layer is opened, it generally fills completely, to the limiting packing characteristic for the intercalating molecule. In any member of a graded family, electrostatic effects cause the layers to space themselves evenly. Thus in a dilute metal such as the 866th stage of Cn^+ HSO_4^- . $2H_2SO_4$ (Ref. 4) many empty layers separate successive filled layers. As a matter of convenience, the sequence is often used to describe which member of any family is under discussion — the first sequence has every layer intercalated, the second sequence has every second layer intercalated and so on. Changes of electronic properties towards more metallic conduction are so striking that one of the most sensitive methods of detecting and following intercalation is to measure the electrical resistance of a conductor of well oriented graphite. As each molecule of an electron acceptor or electron donor molecule enters the solid, it abstracts a charge carrier from the full band, or injects a charge carrier into the empty band of graphite. The consequent

change in numbers of charge carriers per unit volume can be accurately followed in what must be one of the most direct demonstrations of the link between solid state chemistry and electron band characteristics.

Detailed exploration of electronic properties is currently under active progress. In one lecture I can only summarise some of the more striking features of these synthetic metals.

Let me remind you that with well oriented graphite the *anisotropy of electrical properties* is probably greater than in any other crystal capable of conducting electricity. This is readily seen form a brief summary of leading parameters.

	a-axes	*c-axes*
C-C Lattice distance	1.415 Å	3.35 Å
Hardness	$\sim 2 \times 10^{-2}$ mho	> 9 mho
Compressibility	$\sim 2 \times 10^{-10}$ atm^{-1}	2.6×10^{-6} atm^{-1}
Thermal expansion *Coefficient* $\times 10^6$	28	practically zero
Ditto Graphite Nitrate	85	ditto
Ditto Graphite Bisulphate	62	ditto
Ditto Graphite Perchlorate	98	ditto
Thermal conductance	0,06 cm deg K Watt^{-1}	0.0003
Electrical resistivity ohm cm	4×10^{-5}	0.4
Thermoelectric power	about $- 5\mu V/°$	about $+ 8\mu V/°$
Hall coeff. (low fields)	$- 0.04$	$- 0.02$

To first approximation, each carbon hexagon network behaves as a giant aromatic molecule almost though not quite independent of its neighbours distant 3.35 Å from it on either side. To a first approximation likewise, introduction of charge transfer molecules modifies the electrical properties *parallel to the a   axis,* in a fairly predictable way. Charge transfer is not quite unitary; for q molecules brought into contact with an aromatic sheet, fq charge carriers are say, abstracted, where f a factor not far from unity. Elementary theory of electrical conduction shows that for a single type charge carriers the electrical conductivity

$$1/\rho = Ne\mu$$

where N is the number of carriers per unit volume, and μ is their mobility. For synthetic metals based on graphite, the number of charge carriers in all but extremely dilute metals swamps the natural carrier density in the parent graphite, which is about 2×10^{18} per cm^3 at ambient temperatures. Calculations indicate that when n charge transfer molecules are introduced per unit volume, the actual number of charge carriers contributing to electrical conduction is N = fn where f is a fraction near to unity, as stated above.

Synthetic metals of the general formula CnM thus consist of *families,* for which three kinds of conduction characteristics are of general interest:

1. In any family all with the same intercalating M species, at first the layers are so far apart that they can in many ways be treated as independent. Comparing different families, the fraction f will then depend on the completeness of charge transfer from each graphite macromolecule, which is amphoteric, to the intercalated molecules of species M. With electron acceptors, for example (which are known in much greater variety than are electron donors) the most strongly

electron accepting groups are those which form the strongest acids in inorganic chemistry. These give f nearest to unity; weaker electron acceptors would be expected to show smaller fractional transfer. Good p metals are in fact formed by strong acids; for example graphite nitrate C_{24}^+ NO_3^- $2HNO_3$ has a specific conductivity comparable with aluminium.

2. In any family, as the concentration of intercalate increases, filled layers get closer. Various refined measurements of electrical magnetic and other properties indicate that mutual electrical interference between layers becomes perceptible when fewer than about five empty layers separate each filled layer.

On a technical point, this sometimes leads to maximum specific conductivity at about third or fourth sequence. Filling more layers generally continues to lower the resistance of a piece of graphite, but since expansion of the crystal lattice occurs for each layer filled, the specific conductivity tends to asympote beyond the optimum.

Calculations show that were it not for the expansion on intercalation it would be easy to outmatch the best natural conductors, such as gold or copper. However, synthetic metals have a number of other distinctive features not found in natural metals.

3. One of the most striking of these distinctive features is the anisotropy of electrical properties. Until large pieces of stress annealed graphite were available for smooth conversion into large pieces of synthetic metals, valid measurements of electrical resistivity in the direction of the c-axis were not feasible. The apparatus now used in recent measurements has surmounted this obstacle, likewise. Experiments on various families of metals show that intercalation always increases the electrical resistance in the direction of the c-axis, except in the case of the alkali metal atoms which are electron donors. This can be illustrated in various ways, as in the Table. (Ref. 5) gives more details of increase of resistance in the

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direction of the c-axis. On the other hand the specific conductivity increases in the direction of the a-axis.

Effects of intercalation on electrical properties at 295 K

Intercalate	Sp. conductivity increases by a factor (a-axis)	Resistance increases by a factor (c-axis)
ICl	$\times$ 13	$\times$ 1.57
NO_3^- . $3HNO_3$	$\times$ 12	$\times$ 14
HSO_4^- . $2H_2SO_4$	$\times$ 6	$\times$ 13
K	$\times$ 4	3.5×10^{-3} (decrease)

With some families of electron acceptor intercalates, the increase of resistance in the direction of the c-axis ia particularly large. This makes plausible a calculation about the change of resistance of an isolated infinite aromatic hexagon network of carbon atoms, due to the abstraction of electrons. If the intercalate molecules are assumed to have infinite resistance, the increase of conductance in the a-axis direction can be equated to that of the appropriate number of separate conducting sheets, stacked in parallel. With reasonable dimensional assumptions, one can then calculate the specific conductivity of a single sheet of synthetic metal in the a-axis direction. (Ref. 5).

Nominal specific conductivity (Ω^{-1} cm^{-1}) parallel to the hexagon networks.

Intercalate	σ_a (nominal)
K	2.8×10^5
Br_2 or HSO_4^- . $2H_2SO_4$ or $AlCl_4^-$. $AlCl_3$	$\sim$ 6×10^5
ICl or NO_3^- . $3HNO_3$	$\sim$ 12×10^5

This is about the present state of the art. Clearly there are many novel possibilities, that still remain to be investigated. Are there yet any practical applications?

The most obvious one is to look for superconductivity at low temperatures. With the synthetic metals yet investigated at very low temperatures which are caesi um graphite and graphite bisulphate, any conventional superconduction does not set it till about $1°K$. However, other modes of cooperative interaction between the electrons in these layer type solids seem possible. Magnetic and electromagnetic properties warrant further investigation.

Furthermore, it is now feasible to make very large compacts of well alined graphite, with up to 95% graphite and 5% of a suitable polymer. These compacts intercalate quite smoothly to give compacts of synthetic metals. Ultimately this may be important in technological applications of these unusual metallic conductors.

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