Physics of Intercalation Compounds

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With 167 Figures

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Preface

When an area of research is in fast growth, it often happens that no one single journal is to be found where most of the relevant publications are contained. Such is the case of the physics of intercalation compounds, a field which, by sitting at a corner point between materials science, solid-state physics, and chemistry, finds its contributions largely scattered about in the literature. Given these circumstances it is of crucial interest to find a place where the most recent contributions and up-to-date references can be found at once. For intercalated graphite and other similar compounds this role has been played so far by proceedings of international conferences, such as La Napoule (1977), Nijmegen (1979), Provincetown (1980), and Sendai (1980).

The present book is an ideal continuation of this series, as it contains most of the invited and contributed papers of the Trieste International Conference on the Physics of Intercalation Compounds, held in Trieste, Italy during the week 6-10 July 1981.

The main emphasis is on intercalated graphite, though several interesting contributions deal with other materials, such as polyacetylene and transition-metal compounds, or with general problems, such as two-dimensional melting. The book is divided into six sections — Structure and General Properties, Electronic Porperties, Stability and Phonons, Ordering and Phase Transitions, Magnetic Resonance, and Transport Properties — reflecting the main areas of interest, and also broadly the main discussion sessions of the Conference.

We have been guided in the preparation of this Conference by the suggestions of our International Advisory Committee: B. Bergersen, J. Conard, F. F. di Salvo, M.S. Dresselhaus, J. Fischer, P. Fulde, T. Geballe, H.-J. Güntherod, C. Haas, G. Harbeke, A. Hérold, H. Kamimura, S. Solin, and A.R. Ubbelohde. Also L. Reatto, G. Scoles, and M.P. Tosi have helped us with their encouragement and advice. We are very grateful to all these people for their help.

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Part I

Structure and General Properties

Kinetic Problems with Intercalation Compounds

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What follows refers primarily to kinetic problems in *layered* intercalation
compounds. It may be assumed that mobile electrons will be found in any
molecular framework when this contains conjugated valence bond sequences [1]
and that crystals of such compounds are semi-conductors [2]. Graphite may
be regarded as a macromolecular limit of a homologous series of planar fused
ring structures on this chemical basis and behaves as a semi-conductor with
zero energy gap. Already in 1950 we had established that intercalation be-
tween the carbon hexagon layers in graphite by electron acceptor molecules
such as bromine or iodine monochloride, or electron donor molecules such as
potassium, greatly enhances the electrical conductivity parallel to the
layers. However the high conductivity of these first synthetic metals was
considered two-dimensionally. Perpendicular to the layers intercalation
of electron acceptor molecules generally reduces the electrical conductivity
of the parent graphite even further; a recent measurement for graphite ni-
trate showed a reduction of conductivity perpendicular to the layers by a
factor of about 40 [3].

Accordingly, at least to a first approximation, one can discuss the pro-
perties of synthetic metals based on graphite in terms of a pile of 2D macro-
molecules stacked in parallel. The model can subsequently be refined to
allow for weak interaction between the layers whose stacking may be ordered
or disordered. For any one layer, when the electrical conductivity σ_a of
the parent structure can be expressed by the elementary equation $\sigma_a = \bar{n} e \mu$,
intercalation changes this into $\sigma_a = e(n \pm fN)\mu^*$ for the synthetic metal
derived from it. To explain the marked increase of electrical conductivity,
the assumption commonly made follows our original suggestion [4] that
$(n \pm fN) \gg n$, as a result of fractional charge transfer f from N intercalated
molecules per atom of the host structure. Such an assumption encouraged
attempts to increase the conductivity of the synthetic metal by using inter-
calate molecules which give large values of $(n \pm fN)$. Such attempts have
indeed met with some success, in the sense that partner molecules capable
of forming quite strong charge transfer bonds favour the production of high
electrical conductivities. However, no very direct correlation of high
conductivities with strong charge transfer bonding has been established.
It may be at least equally relevant to examine ways in which intercalation
might enhance carrier mobility, e.g., making $\mu^* > \mu$. Such an approach
stresses kinetic problems. It calls for consideration of the various me-
chanisms that can affect charge scattering in any synthetic metal. Unfor-
tunately, any discussion of the principal defect structures that can influ-
ence charge scattering, and thereby affect mobility, has been far from sys-
tematic even for synthetic metals based on graphite, which have been the
most fully explored to date. Accordingly, what follows is illustrative
but should not be regarded as exhaustive.

Because of the versatility of bonding that can be adopted by carbon atoms, solid carbons tolerate an extraordinary variety of bond structures. Even in carbons with well-ordered crystals with, say, more than 95% of their atoms in ideal positions, the phonon spectrum could comprise a much greater breadth than, say, for a simpler inorganic crystal such as copper. Some idea of the range in carbons can be obtained from direct measurements of electrical resistivity of graphites of varying perfection parallel to the basal plane [5]. Other properties such as thermo-electric power or thermal conductivity of carbons [6] can give even more sensitive indications about the defect content of carbons than the electrical resistivity. As has often been stressed, the great versatility of thermal scattering of charge carriers in the parent graphite makes it essential to select material very critically when aiming to produce synthetic metals with optimum behaviour. According to current selection procedures [3] even the best graphites commonly used are far from the ideal limit. However, this somewhat pessimistic warning about defect structures in the parent graphite may not have correspondingly grave implications for ultimate technological superiority of the synthetic metals produced from it by intercalation. On pushing the layers apart, by the process of inserting intercalate molecules, at least some of the defects may become inoperative for charge scattering.

At the present time, various kinds of evidence that layered conductors may be 'improved' by the process of intercalation is fairly plentiful, but mostly circumstantial. It includes studies on the movement of molecules as well as charges. Direct physico-chemical measurements on the overpotential required to begin intercalation for any desired partner molecule indicate that once a threshold has been overcome [7] intercalation proceeds quite easily. There is also evidence that certain molecules which find it difficult to enter directly between the carbon hexagon sheets in graphite may be 'introduced' by prior entry of an easier species [8]. Direct measurements of kinetics of diffusion of partner molecules once they have entered show lateral movement to be surprisingly rapid for certain molecules [9] such as nitric acid.

Our present knowledge about the role of structural defects in electrical conduction of synthetic metals is mainly derived from theories about their chemical bonding, together with measurements on the temperature dependence of their electrical properties. Chemical valence theories show that the atoms in the host structure of a synthetic metal are mainly linked by co-valent bonds. Defects (whose presence can hinder movement of charges, as well as diffusion of molecules through the solid) are basically different from those in close-packed crystals of many natural metals. Carbons tolerate a considerable variety of structural defects. In near-ideal graphites the most important include (the list is not exhaustive):

(a) Carbon atoms at perimeter sites at the edges of each planar macro-molecule. When layered solids are annealed, the principal atomic movements lead to growth of planar macromolecules at the expense of more disordered material. This reduces the proportion of atoms in perimeter sites.

(b) Carbon atoms (such as those displaced by radiation damage) which do not form part of any regular macromolecule.

(c) Planar macromolecules may be stacked parallel in regular sequences or may tolerate various kinds of stacking disorder.

(d) When one or more covalent bonds are omitted from interior positions in a macromolecule, valence bond requirements may no longer allow neighbour-

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ing carbon hexagons to lie in the same plane identically.   Instead, each omitted bond may lie at the nick of a 'claw' defect in the macromolecule, causing it to extend through neighbouring layers [10].

After intercalation of the chosen partner molecules between the layers, these may also locate themselves in distinctive ways at the different kinds of defect sites and may play more than one role in scattering of charge transport.   A very obvious observation is that the temperature dependence of electrical conductivity parallel to the layers is entirely changed, in its general trend, from that of the parent graphite [11a, b].   The resistivity of various synthetic metals decreases on cooling over the range 300-50 K, showing temperature coefficients very approximately in accordance with the Bloch-Gruneisen formula.   It is interesting that the characteristic temperatures θ_R calculated from such data support the view that the main source of electrical resistance parallel to the layer planes arises from thermal vibrations of the intercalate molecules.

Synthetic metal	$\theta_R(^oK)$
C_8K	378
C_8Rb; C_8C_S	296
$C_{24}HSO_4$ $2H_2SO_4$	237
$C_{24}NO_3$ $2HNO_3$	218
$C_{24}NO_3$ $2DNO_3$	168

Lateral thermal vibrations of the molecules in any layer most probably control this kind of thermal scattering for σ_a in the temperature range from 300 K down to at least 3 K.   This suggestion is supported by the observation that a steep decrease of resistivity is observed at the lambda point in graphite nitrates, when the nitric acid molecules in each inter-calated layer take up an ordered pattern [12] (Fig. 1)
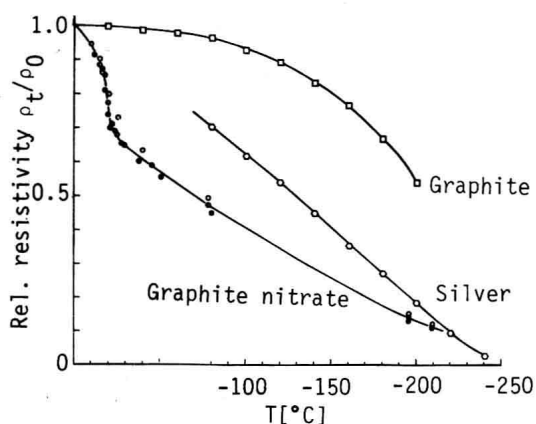
Fig.1. Relative resistivity $\rho t/\rho_0$ (where ρ_0 refers to T = 0°C) as a function of temperature for graphite (□), silver (o), and graphite nitrate (•)

Somewhat surprisingly, there appears to be no clear evidence for any true 'rest resistance' in σ_a associated with non-thermal defects in near ideal graphites, but this may be because they have been specially selected to prepare the best synthetic metals.   In this respect they differ from

natural metals such as copper. And furthermore, as stated, the role of structural defects in charge scattering is probably smoothed out on separating the carbon-hexagon sheets by inserting the partner molecules. However, structural defects of a special kind which traverse several layers may play an important role even in the best near-ideal graphites yet used. Evidence for this suggestion has recently been obtained from accurate measurements of temperature dependence for both σ_a and σ_c, which have been made on material prepared from the same parent graphite. With graphite nitrates of the second stage, logarithmic plots permit reliable estimates of the resistance R_c of specimens perpendicular to the layers, even when the anisotropy ratio σ_a/σ_c is around 10^6. Below the lambda point a remarkable finding is that this ratio proves to be practically independent of temperature, down to at least 70 K. From various considerations [3a, 3b], this seems likely to be due to conduction perpendicular to the layers being predominantly by *extrinsic* leakage paths, which have similar dependence of conductivity upon temperature as for conduction parallel to the layers. This conclusion has so far been verified for two electron acceptor intercalates (with nitric acid and with iodine monochloride). If it can be generalised, it would strengthen the conclusion that ideal graphite free from any defects joining the layers must be truly 2D.

At least two kinds of structural defects 'of type i' have been suggested which traverse neighbouring layers and which may be the site of leakage paths whose presence is inferred from the observed temperature coefficient for the resistivity ratio σ_c/σ_a. 'Claw' structures may arise from the consequences of missing bonds in a covalent aromatic network. Alternatively, a kind of stacking disorder may arise from dislocations traversing neighbouring layers whose presence has been inferred to explain smooth intercalation by successive stages starting with a dilute synthetic metal |13,14|. Defects 'of type i' whose structure traverses more than one layer, which would otherwise be wholly independent, obviously introduce occasional correlation paths between neighbouring layers. As already stated, they are probably responsible for conduction perpendicular to the layers. They may also provide a distinctive scattering mechanism for charge carriers within any layer. The average distance $\overline{x_i}$ between neighbouring defects of this kind in any layer may be small compared with the meanfree path $\overline{\lambda_i}$ for charge scattering within any layer from all mechanisms, except for graphites of unusually high perfection. But with such graphites when $\overline{x_i} \gg \lambda_i$ any trajectories with unusually high velocities parallel to the layers could persist and give rise to 'low scatter' conduction.

Reliable information about mean free paths in synthetic metals is still very scanty. Only a schematic illustration of possible novel effects need be given at this stage (cf [9]). Each conducting layer is a carbon–hexagon macro-aromatic network bounded by layers of electron acceptor molecules on either side. (Fig.2) Within each layer any charge trajectory at near grazing

Acceptor molecules

2D Carbon layer
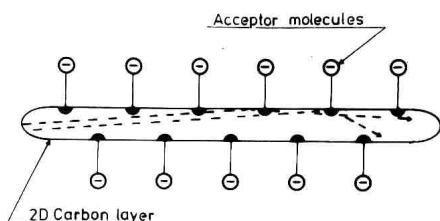
Fig.2. Schematic of carbon-hexagon macro-aromatic network bounded by layers of electron-acceptor molecules

incidence may undergo a kind of total internal reflexion and continue in much the same direction unless it is scattered somewhere within the boundary region. In near ideal conditions, depending on the absence of such scattering, unusually high mean free paths could be attained by a fraction of charge carriers, with unusual electrical consequences.

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Comments on the Stoichiometry in the Metal-Graphite and Metal-Carbon Compounds

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Introduction

A stoichiometric compound can be defined as a chemical species which possesses an experimental composition in good agreement with its "ideal formula".

It is clear that the ideal formula of the G.I.C. cannot be forecast from chemical rules, because their formulae (such as KC_8, KC_{24} and others) cannot be related to the usual valencies of the elements but only to structural data : the G.I.C. are typical "topochemical" compounds.

The in-plane hexagonal unit cell of graphite contains two atoms and its parameter is $a_0 = 1.42 \cdot \sqrt{3} = 2.46$ Å. The surface area of 1 atom is also $(2.46)^2/2 = 2.62$ Å^2. If C_XI (I = intercalant) is the formula of a first stage compound, if S is the surface area of the in-plane unit cell of the intercalated layers, the index x will be :

$$x = \frac{C}{I} = \frac{S}{2.62\ m}$$ in which m is the number of atoms or molecules contained in the intercalant unit cell.

If the parameters of this latter are compatible with that of graphite, (also if the intercalated layers are epitaxial to those of the graphites) x is an integer (or a rational fraction) and the compound possesses a true ideal formula.
If the in-plane parameters of the intercalated layers are incompatible with a_0, the index x can be calculated, but it is only an integer or a rational fraction by chance : the crystallographic formula of the compound is not a true "ideal" formula.
If there is no long-range ordering in the layers of intercalant, the index cannot be calculated from crystallographic data, only an approximate value can be obtained by using the interplanar distance and the molar volumes of graphite and the intercalant in the pure state

$$x = \frac{C}{I} = \frac{\text{molar volume of free intercalant}}{\text{molar volume of free graphite}} \cdot \frac{3.35}{d_i(\text{Å})-3.35} \qquad |1|$$

In the compounds of stage greater than one, a stoichiometric formula needs a regular distribution of the occupied and unoccupied intervals between the graphite layers, so that the stage index n is an integer.

I. Crystallographic and Experimental Formulae of the Metal-Graphite Compounds

I.1 First Stage Compounds

The stoichiometric formulae MC_8 (M = K, Rb, Cs) and MC_6 (M = Li, Sr, Ba, Eu, Yb) correspond to the well known "octal" and "hexal" dispositions of the metal atoms on the adjacent graphite sheets. In the case of the MC_8 compounds, the chemical analysis is in good agreement with the "ideal" formula corresponding to the structure (the difference is 1 or 2 percent). In the case of the MC_6 compounds, the synthesis of pure samples is difficult because of the low vapour pressure of the metals and their ability to form acetylides or interstitial carbides, and the chemical analysis is less certain : the MC_6 formulae have been established more by structural than by chemical studies |2| |3| |4|.

There are no simple and sure reasons to explain the existence of the two kinds of formula MC_8 and MC_6. One can only observe that the metallic radii of the heavy alkalis are more compatible with the octal structure and those of the other metals with the hexal one.

M-M In-plane distance : in MC_8 : 2×2.46 Å ; in MC_6 : 2×2.13 Å

Metallic radii (Å)	Li	Na	K	Rb	Cs	Ca	Sr	Ba	Sm	Eu	Yb
	1.53	1.90	2.35	2.48	2.67	1.97	2.15	2.22	1.81	1.99	1.94
Ionic radii (Å)	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}	Sm^{2+}	Eu^{2+}	Yb^{2+}
	0.6	0.95	1.33	1.48	1.69	0.99	1.13	1.35	1.04	1.12	1.13

However, R. SETTON |5| has shown that the interplanar distance can be calculated by addition of the graphite layers thickness to the ionic diameter of the intercalated metal. It is not very coherent to use the ionic·diameter to calculate the interplanar distance and the metallic diameter to justify the in-plane structure !

For first stage solid solutions $M_{1-x}M'_xC_8$ containing two heavy alkali metals, the theoretical value 8 for the ratio C / M+M' is also in good agreement with the analytical data |6| ; x can vary from 0 to 1.

Other stoichiometric species containing two metals are the $KHgC_4$ and $RbHgC_4$ ternary compounds, which contain triple metallic layers. The ratios C/K or C/Rb = 4 correspond to the octal epitaxy of two alkali metals layers on the graphite sheets. The ratios Hg/K and Hg/Rb = 1 can be explained by the complete occupation of the prismatic sites between the alkali metal atoms by mercury ones. One can also observe that the free alloy KHg is a defined compound but not RbHg |7|.
Solid solutions $K_{1-x}Rb_xHgC_4$ exist, in which x can vary from 0 to 1.

On the contrary, the $MTl_{1.5}C_4$ ternaries (M = K, Rb) |8| contain thick metallic layers without in-plane long−range ordering : there is not any structural explanation for the rather exact experimental value of the ratio C/K = C/Rb = 4 which have been obtained by reaction of graphite with potassium - thallium and rubidium - thallium alloys of different compositions. Nor are there any explanation for the value Tl/K = Tl/Rb = 1.5, because the free alloys $KTl_{1.5}$ and $RbTl_{1.5}$ are not defined compounds. Thus,

the formulae $MTl_{1.5}C_4$ are not true "ideal" formulae, and the indices are on-ly approximate values ?

On the other hand, it is remarkable that the compound $RbTl_{1.5}C_4$ exists under 2 forms, which differ by their interplanar distances :
12.65 Å for the α metastable phase and 13.40 Å for the β stable phase.

I.2 Stages Higher than One

Among the metals which form intercalated layers with an hexal structure, only lithium leads to defined high stage compounds ; the stage 2 has been prepared with a stoichiometric formula LiC_{12} in the presence of a small amount of LiC_6, but its formula can vary from LiC_{12} to LiC_{25} |2|. Higher stages are not stoichiometric |9||10|.

It is well known that the heavy alkali metals do not form compounds of a second stage with an octal structure : for a long time the dodecal la-cunar structure proposed by RUDORFF and SCHULZE |11| and leading to the ge-neral formulae MC_{12n} for the compounds of stage n > 2 were generally accep-ted. Unfortunately, recent studies of S.A. SOLIN and others, using diffuse X-ray scattering |12| |13| |14|,concluded that at room temperature the inter-calated heavy alkali metals form liquid-like layers without long range orde-ring ; the study of these layers by M.S. DRESSELHAUS and co-workers, using the transmission electron microscope, leads to a rather different conclusion |15| : several kinds of organized domains would coexist in each layer. This observation seems to be in agreement with the previous study of PARRY |16| concerning the Cs-G system. In any case, these different kinds of organiza-tion cannot lead to stoichiometric formulae. In the case of potassium, gra-vimetric and analytical data are in rather good agreement with the formula KC_{24} for the second stage. However, we do not know
- if the composition depends on the conditions of synthesis
- if the composition is the same for the compounds of K, Rb, Cs.

According to M.S. DRESSELHAUS |15|, the in-plane surface area of the metal can be calculated by dividing the volume of the free metal unit cell V_m by the M-M distance, which is $a \cdot \sqrt{3} / 2$. This calculation leads to the formulae $KC_{24.1}$ $RbC_{27.76}$, $CsC_{32.26}$, which give an order of magnitude of the expe-rimental composition, but cannot be considered as "ideal" formulae.

By lowering temperature, an important structural evolution is observed, including phase transitions at the temperature generally called T_u and T_ℓ ($T_u > T_\ell$) and leading to higher degrees of organization.

Among the ternaries of stage 2, the mercurographitides $MHgC_8$ (M = K, Rb) and the alkali metal-thallium compounds $MTl_{1.5}C_8$ (M = K, Rb) seem to contain the same type of layers as the first stage ones. So the former are stoichio-metric and the latter are not true stoichiometric phases.

The sodium-barium-graphite compounds of stage 2 and 3 |17| offer another kind of structure. The triple metallic sheets (one layer of barium between two layers of sodium atoms) are biperiodic, but the parameter a = 6.36 Å of the unit cell is not compatible with the graphite one. The corresponding ratio C / Na+Ba for a second stage is 8.92 and it is only an approximate agreement with the experimental values of about 7-8.
On the other hand the ideal ratio Na/Ba is 2, but, in fact, the experimental values vary from 1.6 to 5, probably by partial substitution of one metal for the other.

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