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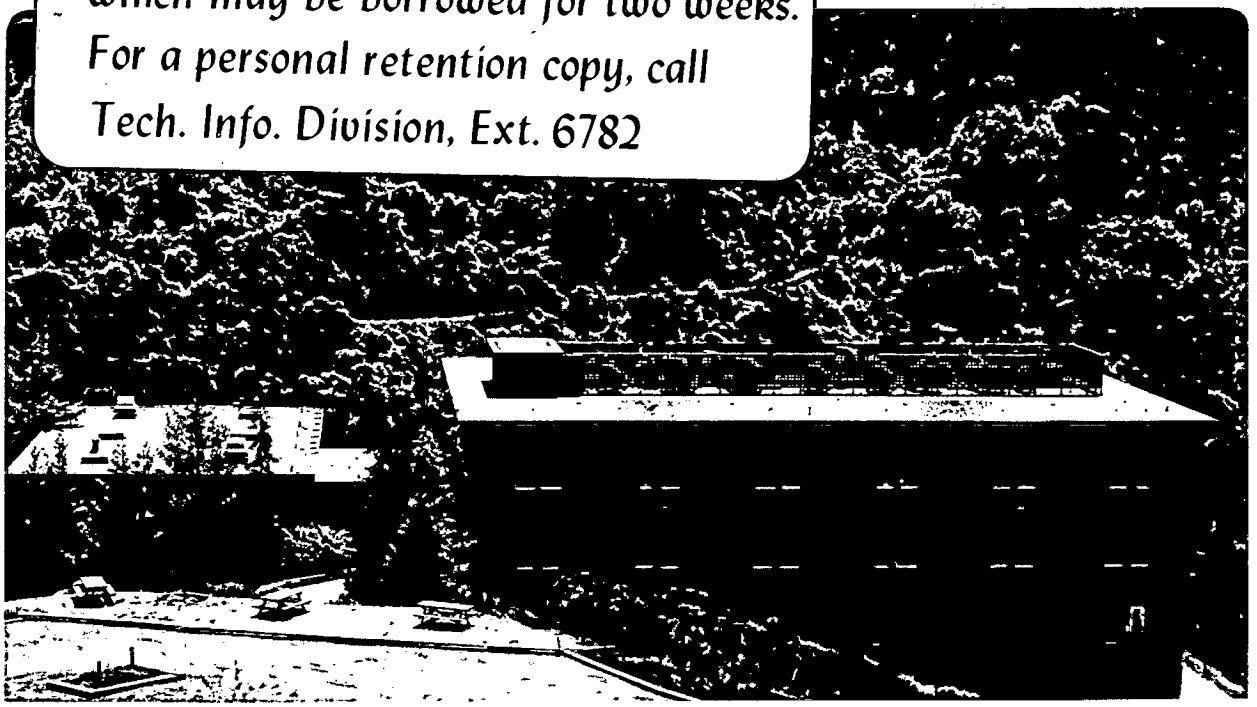

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GRAPHITE CHEMISTRY

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CONTENTS

I. INTRODUCTION

The first intercalated compound, graphite sulfate, was described by Schauffaütl in 1841.[1] Intercalation of graphite involves penetration of guest species between the carbon layers with consequent expansion of the graphite in the c axis direction. Intercalation usually proceeds in stages (see Fig. 1). The region between adjacent carbon layers, which may be occupied by guest species constitutes a gallery. The known intercalating reagents are numerous. They range from strong oxidants to powerful reductants.[2] The metallic electrical conductivity of many of the intercalated graphites and the possibility that they might be used to store and transport electricity, has quickened interest in them. These compounds also pose important fundamental questions, which advances in synthetic techniques, physical measurements and theory have made timely. There have been several comprehensive recent reviews devoted to graphite intercalation compounds, of which those by Herold,[3] Ebert,[4] and Ebert and Selig[5] deal thoroughly with structural and chemical aspects of the compounds. A review by Fischer[6] is from the perspective of a physicist. There have also been two recent conferences [7,8] devoted to intercalation compounds of graphite, the conference proceedings of which collect much of the current work in the field. In this review we shall not provide an exhaustive survey. Instead, we shall select certain systems which have been studied extensively. Our aim is to indicate principles which may be of value for future research directions in this field.

Many of the known intercalants of graphite can be represented as either oxidants or reductants of graphite. Two of the following sections of this review therefore deal with species which can be placed in either of these categories. At the outset, however, it is appropriate to consider features

of graphite itself, which are pertinent to intercalation, then some general features of graphite intercalation compounds.

II. GRAPHITE

A. Nature of the Material

The degree of perfection of the graphite used in the preparation of intercalation compounds, and even the size of the graphite crystallities have important influences on synthesis. Hooley[9] has documented such influences and has demonstrated that graphite specimens of a given quality, which are thin in the c axis direction undergo intercalation with a lower threshold activity of intercalant than do thicker specimens. Also, for oxidizing intercalation, those carbons which are highly imperfect (as a consequence of much cross-linking of the layers) do intercalate less readily than those which are more perfect. On the other hand, for reducing intercalants, such as the alkali metals, the available experimental evidence indicates that inter-layer cross-linking appears to aid intercalation. This has been attributed to lowering of the Fermi level by the cross-linking.[3]

It must be remembered that when intercalation occurs, some of the defects of the parent carbon may carry over into the intercalation compounds.[3] Such defects can have gross impact upon physical properties such as electron transport. Ubbelohde has discussed such effects on charge-scattering[10] and the ordering of intercalants. In carbons in which there are many linkages between carbon layers (such linkages are referred to by Ubbelohde[10] as 'rogue bonds') intercalation of bulky species can only proceed if such bonds are broken (indeed, Ubbelohde[10] has suggested that reversible intercalation could provide for increasing the perfection of graphite by removing 'rogue' bonds in this way). Carbons in which much 'rogue' bonding occurs are usually

obtained by the pyrolysis of solid organic compounds and include glassy carbons and polyvinylidene cokes. These are often highly porous however, and physical absorption can readily occur in them, and this may occasionally be confused with intercalation. The pyrolytic graphites made by the pyrolysis of liquid organics[11] can also be rich in defects, unless they have been well annealed at $\sim$ 3000°C. The highest quality graphites, and the most satisfactory for intercalation studies, are obtained by the pyrolysis of small molecule hydrocarbons at $\sim$ 3000°C.[12] High temperature annealing again improves crystallite perfection.

B. Bonding in Graphite

A fragment of the infinite two dimension network of sp^2 hybridized carbon atoms of a perfect graphite is indicated in Fig. 2(a). The bonding of the carbon atoms of the planar sigma-bonded layer (ab plane) is enhanced by the π bonding, derived from the combination of the p_z orbitals provided by each carbon atom. Since each pair of π electrons in the graphite carbon layer contributes to the bonding of three carbon-carbon linkages, whereas in benzene such an electron pair enhances the bonding of only two C-C linkages, the bonding in the graphite layers is not as strong as in benzene. The in-plane bonding in a layer of graphite is, however, stronger than the C-C bonding in diamond. Indeed, the carbon layers are physically and chemically robust and appear to remain planar even when reduced or oxidized. The addition of electrons to the conduction band (anti-bonding π orbitals) or the removal of electrons from the valence band (π orbitals) decreases the bonding in the layers. Small changes in the ab plane dimensions therefore do occur in association with intercalation.[3] In all of the high quality graphites, (Fig. 2b), the effective thickness of a carbon layer is always close to 3.35 Å.

Since the layers are merely van der Waals bonded, this distance represents the effective van der Waals thickness of such sheets. Electron oxidation or reduction of the carbon layers does not appear to have much effect upon this thickness.

C. Band Structure of Graphite

Since, in most instances, the intercalation of graphite does not lead to gross changes in the carbon layers, it is useful, at lease as a first step, to use the band structure of graphite as a basis for understanding the electronic properties of the intercalated graphites. The first detailed discussion of the bands generated by the combination of the p_z orbitals of the carbon layers was given by Wallace[13] in 1947. There have been a number of significant refinements since then which are important in accounting for optical, magnetic, and electrical properties.[14, 15] As far as intercalation chemistry is concerned, at lease at the outset,it is sufficient to treat the band structure of an isolated carbon layer, i.e., deal simply with the two dimensional network, for which the unit cell and Bravais lattice are shown in Fig.3(a). It must, however, be remembered that the three-dimensional pristine graphite situation is more complex than the one we are about to discuss. A major difference is that, in the three-dimensional case, the layer-layer interactions, although merely van der Waals, do result in overlap of the lowest band (the valence band) and the band next in energy (the conduction band). It is this overlap[16] of approximately 0.04 eV, which produces the semi-metal character of graphite. The overlap means that the conduction band contains electrons and the valence band has holes, each with a density of $\sim 10^{-4}$ carrier/carbon atom. Both carriers contribute to the electrical conductivity. The effect of oxidation or reduction on the band occupancy of the isolated carbon layer is shown in Figure 3(b).

For the single layer, as shown in Fig. 3(a) the Brillouin zone is a hexagon. The combination of the p_z atomic wave functions gives the two π bands (the valence band and the conduction band) which are degenerate only at the six Brillouin zone corners.[13] There is no overlap of these bands, nor is there a band gap. At 0° K the valence band is filled and the conduction band empty, therefore, the Fermi level is at the point of contact of the bands. [See Figure 3(b).] The width of each of the π bands[15] is about 20 eV and since in the three-dimensional graphite case, the energy of interaction of the layers is only about 0.5 eV, the overall character of the π bands is not changed much in the formation of the three-dimensional structure, although the previously mentioned slight overlap, 0.04 eV, is of course of profound importance.

The two-dimensional model for the band structure may be a satisfactory approximation for first-stage graphite compounds, when the intercalants are large closed-shell species, which provide for no effective overlap of orbitals with the p_z orbitals of the carbon layers. It may, therefore, be valid for the graphite salts in which stable anions such as NO_3^-, $C\ell O_4^-$, HSO_4^-, and AsF_6^- are intercalated between layers which bear net positive charge. Certainly the measure of the anisotropy of the electrical conductivity given by σ_{ab}/σ_c indicates[17] that such salts are more two-dimensional in conductivity than is pristine graphite itself, where experimental values for σ_{ab}/σ_c range from 10^2 to 10^5 depending upon the quality of the graphite.

In the cases of graphite compounds where the intercalants possess vacant or partially filled orbitals, their overlap with the p_z orbitals of the carbon layers will result in chemical bonding. This must raise questions concerning the validity of the two-dimensional band structure as an approximation for such systems. It therefore is unlikely that such a simple model

can be applied to the graphite compounds of the alkali and alkaline earth metals. The enhancement of c axis conductivity in these compounds, relative to pristine graphite, (they approach three-dimensional metallic behavior) points to such an overlap of valence orbitals of the intercalant and the p_z orbitals of carbon.

III. SOME GENERAL ASPECTS OF GRAPHITE INTERCALATION COMPOUNDS

A. Structural Features

The characterization of the guest species in graphite intercalation compounds is a major experimental challenge. The metallic nature of most of the intercalation compounds means that structural studies based on longer wavelength electro-magnetic radiation are limited, because it ordinarily does not penetrate beyond the surface layers. Thus, infrared spectroscopy usually samples the surface, whereas with the shorter wavelengths available in Raman spectroscopy, depths up to $\sim$ 1000 Å of the sample can be excited.[18] Similar difficulties may arise in NMR spectroscopy although the information from the surface regions is often valuable.[19] Highly penetrating hard x-rays can measure bulk structural features, and, in the neighborhood of an absorption edge, diagnostically valuable chemical shifts[20, 21] and EXAFS data can be obtained.

It is often difficult to obtain well-ordered single crystals of graphite intercalation compounds, therefore high-quality structures are rare. Structural information from 00ℓ data is relatively common however, since structural ordering with respect to the c axis is easy to maintain if the graphite used in the preparation was a single crystal or a specimen of highly oriented pyrolytic graphite (HOPG).

Many of the graphite intercalation compounds have well-ordered

structures at the microdomain level, but highly disordered structures can also arise. In stages higher than the first, adjacent carbon layers have half the carbons eclipsed as in graphite itself (Fig. 2(b)). Their relative disposition can be conveniently represented as AB (or ABC). Those graphite layers which contain an occupied gallery are commonly eclipsed. If an intercalated layer is represented by a vertical stroke, a shorthand representation for a fist-stage compound, with the carbon layers eclipsing in the c axis direction, is A|A|A... A second-stage compound might be AB|BA|AB, etc., and a third stage ABA|ABA|ABA... .

B. Energetics of Intercalation

Since the energy of binding of carbon layer to carbon layer in graphite[22] is approximately 1.5 kcal $mole^{-1}$, the separation of the layers on intercalation involves work. Formation of a compound also commonly involves a decrease in entropy, which can be sizable for gaseous species becoming guests in a highly-ordered arrangement. The interaction between guest and host must, therefore, meet these enthalpy and entropy burdens, if the compound is to be thermodynamically stable. In many compounds, this energy comes from the Coulomb interaction consequent upon the guest species either oxidizing or reducing the host.[23] Graphite is relatively easy to oxidize or reduce. For the graphite compounds derived from the heaviest alkali metals (Section IVA) and for those containing hexafluroanions (see Section VC), thermodynamic factors have been quite well defined. Thermodynamic factors appear not to be the only obstacle to synthesis, however.[9]

C. Mechanisms of Intercalation

Studies related to the mechanism of intercalation have been carried out on very few systems; that of bromine intercalation being the best documented.

Hooley[9] was the first to demonstrate that Br_2 intercalation is determined by basal plane adsorption--no intercalation of bromine occurs if the basal planes are covered with wax. He also showed that the regions nearest the basal planes open first, the stage obtained depending upon the partial pressure of the intercalant. The first stage is produced at the highest activity.

A low energy electron diffraction (LEED) study[24] indicates that a monolayer coverage of the (001) surface with bromine precedes gallery opening. An x-ray absorption study[25] indicates that molecular bromine lies flat on the surface at pressures corresponding to near monolayer coverage. The bromines lie 2.53Å above the carbon plane with a Br-Br distance of 2.31Å. Polarized EXAFS measurements[26] on dilute intercalated samples show two different Br-Br distances at 2.34 and 2.53Å. The latter distance is consistent with the Br_3^- ion.

Young has postulated[27] an electronic effect to explain the action of adsorption of Br_2 on the (001) plane in opening a gallery as far away as 700 Å from that surface. Filling of that gallery causes others to open both closer to, and further from, the basal plane. Hence gallery opening progresses from the basal plane.

The domain model first proposed[28] by Daumas and Hérold, which is represented in Fig. 4(a) has received experiment support from direct imaging studies of the graphite|$FeCl_3$ system.[29] The model provides for an understanding of how the changes in stage (e.g. three to two) can occur with such facility. This model allows that most real graphites have ramps from one gallery to another, by which the guest species can be sent from one to the other. With this model,

and from consideration of the effects of elastic coherency strains, Safran, et.al [30] have provided an explanation for staging. In their analysis, each guest is represented by a couple of forces with zero moment, which extend the gallery from the original height of 3.35 Å. These elastic dipoles are illustrated in Fig. 4(b). When two such dipoles are situated as in A, they repel one another, while those in position B, attract. Thus guest islands are formed, which in their stacking along the c axis, show the typical staging periodicity (Fig. 4(a)). These strains drive a mixed-stage or randomly-staged crystal to pure-stage ordering.

It seems quite probable that all intercalation into graphite involves adsorption of guest molecules, initially on the basal plane (001), accompanied by electron transfer between the guest and graphite, with subsequent steps being much the same as described for bromine.

D. Electronic Properties of Graphite Intercalation Compounds

Most studies of electronic properties of graphite intercalation compounds have been made to further our understanding of their highly anisotropic metallic conductivity. In spite of its over-simplifications, the Drude model[31] provides for the relationship of the specific conductivity σ to the number of carriers n. The relationship is:

$$\sigma\left(\frac{\text{length}}{\text{ohm x cross-sectional area}}\right) = \frac{ne^2\tau}{m^*}$$

τ being an averaged scattering or relaxation time, and m^* is the effective mass of the predominant charge carrier, defined by

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}$$

where the E vs k contour of the band structure is known. Thus one has the variables n, τ, m^*, and the cross-sectional area of the current flow to measure, in order to interpret the experimental conductivities of these intercalates.

Intercalation affects both m^* and n. Knowledge of the number and charge of the intercalated species gives the number of electrons withdrawn from or added to the graphite. From knowledge of the structural unit cell, the Brillouin zone can be derived. Band theory calculations, with such information, can, in principle, yield n and m^*. The dependence of the electron energy, E, upon the vector k is illustrated for the two-dimensional Brillouin zones of graphite in Fig. 3(a). As we have seen, the effective mass of the charge carrier, m^*, is defined in terms of those quantities. The only unknown in this simple Drude model is τ, which can only be treated as an empirical factor (the value of which may be expected to change upon intercalation). Thus, in virtually all cases, conductivity measurements have not been interpretable in terms of microscopic parameters.

Comparisons of published data among several groups and among various compounds leads to different values of these parameters even for nominally equivalent material. Many measurements have been made using different qualities of graphite, which makes comparisons of σ difficult due to the unknown impact of defects on τ. Most investigators minimize, but cannot eliminate, this effect by measuring each piece before and after intercalation,

to obtain the relative change in σ. A further difficulty occurs when different techniques for measuring σ are used. Most early workers used 4-probe bridge measurements.[32] Zeller, et al,[33] have shown that a contactless radio frequency method eliminates the consequences of attack by the reactants on the electrodes, and the effects of non-uniform current flow. This rf method seems to be the preferred means for measuring the large in-plane conductivities of many oxidized graphites. The contactless measurements also indicate that the earlier σ_{ab} values from 4-probe techniques may have been under-valued.[34]

The conventional σ values for intercalation compounds of course involve the cross-sectional area across which the carrier flux passes. For σ_{ab}, this involves the thickness of the sample along the c axis. However, this cross-sectional area grows as the c axis expands and the unit area has fewer carbon layers. Most investigators re-normalize their σ_{ab} for various stages so as to always maintain a unit cross-sectional area. Thus, their units are $(\Omega^{-1}\text{-cm}^{-1})$. However, if the carriers are primarily located in each graphite layer (as appears to be the case for intercalation compounds of oxidized graphite) it is useful to compare the σ_{ab} normalized to a constant number of carbon layers. This can be obtained conveniently by multiplying the σ_{ab} value by the relative change in thickness t/t_o as measured along the c axis.

IV. INTERCALATION WITH GRAPHITE REDUCTION

A. Binary Systems

The compounds of graphite intercalated by the alkali metals are among the most studied of graphite materials. By comparison, the alkaline earth, lanthanide, and transition metal compounds are little investigated. To our knowledge, only one review has been devoted solely to the alkali metal intercalates,[35] although they have been thoroughly discussed in other major reviews.[36]

The synthetic methods used in the preparation of the alkali metal intercalates distinguish two classes. The heavier metals K, Rb, and Cs react readily with graphite at 200°, or less, using a standard two-bulb technique. Lithium reacts only at higher temperatures or pressures, and lithium carbide is a common impurity in the product. The sodium compound is difficult to make directly and is relatively poorly characterized. The distinction between the two groups (K, Rb, Cs) and (Li, Na) has brought speculation[37] that the ionization potentials of the gaseous atoms provide the basis for the distinction between the two classes. The ionization potentials (in eV) of K (4.34), Rb (4.18), and Cs (3.89) lie below the electron affinity of graphite, which has been estimated[38] to be 4.6 eV, while Li (5.39) and Na (5.14) lie above the affinity of graphite.

The conditions of synthesis of the alkaline earth[39] (Ca, Ba, Sr) and lanthanide (Eu, Yb, Sm, Tm)[40] intercalates parallel the conditions for lithium intercalation. Temperatures of 500-600° for several weeks are required to reach first stage. The first ionization energies of all these metals lie above the electron affinity of graphite.

The distinction between the two metal classes M (K, Rb, Cs) and M' (Li, Na, Ca, Ba, Sr, Eu, Yb, Tm, Sm) in synthetic conditions also carries over to their composition and staging. The first-stage C_8M and higher-stage $C_{12n}M$ compositions contrast with the first-stage C_6M' (except Na). The second-stage lithium compound appears[3] to be of variable composition $C_{12}Li$ - $C_{18}Li$. No pure higher-stage materials C_xM' have been obtained.

Table I gives the structural parameters for these compounds. The experimental values for the unit cell c dimensions yield carbon layer-guest-carbon layer distances, I_c, which are compatible with cationic guests. Indeed the effective guest diameter obtained by subtracting a carbon layer thickness of 3.35 Å from I_c is often less than the diameter of the guest

as a cation. This may simply be a consequence of the guest species nestling in the centers of hexagons of the carbon layers. The heavy alkali metals do not form a simple one-gallery-height c-spacing in the C_8M composition. The unit cell within a gallery is shown in Figure 5. This unit cell allows for any of four sites to be occupied. In low temperature forms of C_8K and C_8Rb, all four sites are occupied sequentially in consecutive layers, such that the c-spacing is four times the interlayer distance. This c-axis ordering is denoted AαAβAγAδ, where the A.A.A represents eclipsing graphite layers. In C_8Cs, however, it is claimed that only three of these sites are occupied, the layering sequence being AαAβAγ. In all C_8M compounds, the c-axis ordering changes as a function of temperature, and at high temperatures ordering from on gallery to the next is lost. In the C_6Li compound, the unit cell provides three equivalent sites (Figure 5). Apparently the Li occupies one site throughout the structure and the c dimension equals the interlayer spacing. Parry and Nixon[41] have examined higher stage $C_{12n}M$ compounds, and found that graphite layers eclipse one another across a metal gallery, while they are staggered, as in graphite, when the carbon layers are adjacent.

The alkaline earth and lanthanide intercalants are just beginning to be characterized by X-ray diffraction studies. Some structural information on the C_6M compounds (M = Ca, Sr, Ba, Sm, Eu, and Yb) has been obtained.[39,40] It seems that the metal layer sequences may be AαAαAα (as for Ca) or AAαAβAαAβ... (as for Sr, Ba). It is noticable from Table 1 that the Eu appears to have an effective size closer to that of Sr than Ca, whereas Yb is like Ca. These two lanthanides have the most stable M^{2+} oxidation states among the lanthanides. Magnetic susceptibility measurements on these compounds have not been made to confirm that the metals are M^{2+}. In all these cases, though, it is doubtful that the metal has been completely oxidized by

the graphite. Metal-metal bonding may well occur between the guests in these compounds.

B. Ternary Systems

Knowledge of ternary systems has come chiefly from the work of Hérold and his coworkers.[42] Intercalation of mixed metals from molten alloys include Ba-Na, and pair-wise alloys of Na, K, Rb, Cs. In the sodium alloys, the presence of a Na within the gallery is only temporary. Upon prolonged contact with the alloy, the Na is eventually replaced by other metal.[43] This behavior parallels the apparent instability of C_xNa compounds. In the phase diagrams for the binary alloy intercalates, the interplanar spacing remains similar to that for the compounds of the pure components near the metal-rich extremes.[44] Over a particular composition range, the interplanar spacing changes by several tenths of an angstrom, and in this same range, the magnetic susceptibility shows an anomalous spike. It may be that some ordering or clustering of the dfferent alkali guest species is involved in this behavior. Structural studies which focus on the question of guest arrangement should clarify the situation.

In the graphite Na-Ba system, at a composition C_8Na_2Ba, the gallery height and composition imply[45] that a single gallery contains a layer of Ba atom, sandwiched between layers of Na atoms, this triple layer being bounded by the graphite layers. Analogous compounds involving Hg sandwiched by K or Rb (first-stage C_4KHg, and second-stage C_8KHg) are also known.[46] Herold[3] has assigned formal charges C^- K^+ Hg^- K^+ C^- to the metal layers (although metal-metal bonding would eliminate the presence of isolated Hg^-). Perhaps the Hg atoms sandwiched between the alkali cations are somewhat positive. Positively charged mercury would be smaller than neutral or negatively charged mercury.

Another class of ternary compounds is the graphite-alkali-hydrogen compounds. A first-stage C_8K, when treated with H_2, forms a second-stage material of composition of $C_8KH_{0.66}$. In the latter, a gallery contains a K-H-K layer sequence.[47] The action of further alkali metals on this product produces a new "first stage" where the added metals enter the empty galleries. Within these galleries, the newly added metal forms the usual C_8M type gallery. Lithium removes some of the hydrogen as LiH, without intercalating, while Na does not react. Higher stage $C_{12n}K$ can also be "hydrogenated" to form compounds with K-H-K layers. For these sandwiched hydrogen compounds. it seems likely that the hydrogen is hydridic.

A third class of reduced ternary intercalation compounds is derived from solution (NH_3, THF, aromatic compounds) of metals (alkali, alkaline earths, lanthanides, aluminum).[42] In these compounds, the solvent molecules as well as the strongly-reducing metals are intercalated. The interlayer spacings in these compounds appear to be determined primarily by the dimensions of the intercalated solvent molecule. An example is the compound in which both benzene and sodium are intercalated together.[48] Two models have been proposed. In one, the benzene ring lies adjacent to a graphite layer and parallel with it. The sodium ions are assigned as sandwiched between the benzene and the other graphite layer. In the second model, the plane of the ring of the benzene molecule is set perpendicular to the graphite layers. The latter arrangement is a satisfactory one, if, as seems reasonable, the benzene rings participate in bearing the negative charge. Thus the negatively charged

benzene rings will screen the sodium ions from one another. Some tilting of the rings from the perpendicular would still provide for this however, and could give better packing.

The recent discoveries of the mercury and hydrogen ternaries with alkali graphites are surprising, and pose important questions concerning their formulation and bonding. It seems likely that many more such novel combinations with graphite will be found.

C. Electronic Properties of Reduced Graphite Intercalates

The electronic properties of the alkali-metal intercalates have received much attention. The sizable diamagnetic susceptibility of the graphite is lost and a small Pauli paramagnetism arises.[49] Electrical conductivity increases ten-fold in the ab plane, and approximately two hundred-fold along c at the first stage.[28,50] The a-axis conductivity levels off[51] in the region of the 4th to 8th stage and apparently decreases slightly for the heavy alkalies. However, correcting the conductivity, for the expansion in the c axis direction which accompanies intercalation, shows that the conductivity per plane is nearly constant, (see Table II). The c-axis conductivity increases monotonically up to saturation.

From Raman studies of the carbon-layer vibrations, Solin[18] has provided persuasive evidence that the charge transferred to the carbon, from the heavy-alkali guests, is largely confined to the layers containing the metal-atom layer.

One of the more significant measurements has proved to be that of the Hall coefficient of these materials.[52] In the reduced graphite e.g. $C_{36}K$ the R_H is negative in sign, indicating that electrons are the carriers.

The negative sign also is clear electronic evidence that the graphite is reduced. There exists some evidence that R_H for C_8K changes sign at very low temperatures (below 77 K).[53] This evidence gives some support to the view that C_8K may actually be a semimetal with both electron and hole carriers. However, further work is needed to confirm this proposal.

In order to measure the density of states in the first-stage compounds, magnetic susceptibility[54, 55, 56] and heat capacity experiments[55,56] have been performed. The density of states value, derived from heat capacity measurements, differs by a factor of two from that obtained from magnetic susceptibility data. The heat capacity data appears to be in better agreement with band calculations.[57] Electron-phonon coupling has been invoked to explain the departures from theoretical expectations.[55] A strong coupling of the electrons with the lattice is clearly occuring below 1° K, when these first-stage compounds become superconducting.

In summary, the electronic properties of the C_xM compounds are consistent with reduction of the graphite. In the first-stage material, there appears to be some anomolous electronic and spectroscopic behavior which merits further investigation.

V. INTERCALATION WITH GRAPHITE OXIDATION.

A. Graphite Salts from Strong Mineral Acids.

Preparative and structural work by Rudorff and his group[58,59] laid the basis for the more recent studies of graphite salts containing strong acid anions. However, the impetus for current activity in the field sprang from the discovery of the high ab plane conductivities of these salts,[60,61] that came from the work of Ubbelohde and his co-workers, following their successful production of large pieces of highly oriented graphite, bearing relatively few defects.

The salts can be prepared by chemical oxidation (e.g. by nitric acid) but anodic electrochemical oxidation has also been used. The latter has permitted accurate coulometry[60,61] to be applied to the synthesis of the salts containing HSO_4^-. Since such oxidations in mineral acids also result in the neutral mineral acid molecules being intercalated, coulometry permits determination of the fraction of the guests which are charged. From the mineral acid preparations the typical formulations are $C_{24}^+X^-2HX$ ($x=C\ell O_4^-$ or HSO_4^-), and for nitric acid $C_{24}^+NO_3^-3HNO_3$. There appears to be no reason why any strong-acid anion (except, perhaps, very bulky ones) should not be intercalated into graphite. If the neutral acid is present it will also be intercalated.

Data from some mineral acid salts are given in Table III. They show that the occupied gallery height, I_c in the salts is much the same for perchlorate, bisulfate and some of the nitrates. Indeed the value of ~7.9A, and the stoichiometries, are compatable with a rather close-packed double layer of oxygen ligands.

For the bisulfate and perchlorate this implies a close-packing of the 'tetrahedra' according to one or more of the models shown in Figure 6(a). It is also clear that if planar nitrate groups are present in the galleries, they cannot be parallel to the carbon layers, in those salts for which $I_c \approx 7.8$A. Recently Touzain [62] has used 00ℓ powder data to support the model represented in 6(b). He concludes that the stoichiometry should be $C_{4.3n}H_xNO_3$ (x=5/6) in these materials. The newly described[63] nitrates having I_c=6.55A, obtained from the I_c=7.8A material, by desorbtion of intercalant, appear to obey a staging formula $C_{8n}(H)_xNO_3$ (x<1 but not defined). This gallery height is consistent with planar NO_3 species lying parallel to the carbon layers. Figure 6(c) shows possible ordered arrangements. The conversion of I_c=7.8 to I_c=6.55A material must involve loss of HNO_3. As these neutral molecules (which serve as dielectric spacers for the NO_3^- ions) leave the galleries, the repulsive interactions of the anions should favor the structure in 6(c). A further factor favoring a small I_c, when there is a large anion fraction of guests, is the increased coulomb attraction between guests and carbon layers.

The $C_{8n}X$ formulation is the same as that observed[20,64] in the close-packed first stage hexafloride-intercalated C_8MF_6 (M=As, Os, Ir), where, of course, two such layers of relatively close-packed guest ligands (F and O are similar in size) are required in place of the single layers seen here. The x-ray diffraction studies of Rudorff[59] had indicated that the guest disposition in one gallery is sensed by guests in neighboring galleries. Thus the bisulfate has the

structure shown in Figure 7, and this and other ordered arrangements have been observed in other salts.

From coulometric studies[60,61] of bisulfate, perchlorate and nitrate intercalation, done in concert with Hall coefficient measurements, Ubbelohde and his co-workers have demonstrated the p type of conductivity of these materials. They have also shown that the salts are very good ab plane conductors, having specific conductivities comparable with or higher than that of aluminum. The conductivity in the c-axis direction is usually much lower than in pristine graphite, although the values clearly depend upon short-circuiting by defects which link the carbon layers. Indeed, as Ubbelohde has discussed,[10] defects are an important source of scattering of the charge carriers. All other things being equal, increase in the perfection of the graphite salts increases the ab plane conductivity and decreases that in the c-axis direction. An approximately tenfold increase in σ_{ab} has been noted[10] for graphite nitrate, cooled from room temperature to 63°K. This has been attributed to a decrease in the carrier scattering associated with a 'freezing in' of the guest species in their lattice sites.

Much higher positive charges in the carbon layers can be obtained by avoiding the use of mineral acids in the synthesis. Thus, peroxydisulfuryldiflouride, $S_2O_6F_2$, will oxidize graphite spontaneously[65] to produce a material of approximate formulation C_7SO_3F. This is an inferior ab plane conductor to related material $C_7(SO_3F)_{1/3}(HSO_3F)_{2/3}$ made by treating graphite with an appropriate mixture of $S_2O_6F_2$ and HSO_3F. It is not clear why it

is so. Comparison of x-ray diffraction data from the two materials, made from the same parent carbon, shows that the acid-containing compound is highly crystalline and that C_7SO_3F is not. In the acid salts, proton mobility[66] must result in haphazard and fleeting charging of the guest species. This, and the relatively low positive charge per carbon layer, may be important to the preservation of undistorted hexagonal carbon layers. Low conductivity and poor crystallinity of C_7SO_3F may, however, signify a distortion of the carbon layers.

Low conductivity and poor crystallinity have also been observed[64] in $C^+MF_6^-$ salts (See V C.)

B. Intercalation of Oxides.

Claims for the intercalation of a number of oxides into graphite have been advanced,[3,5] but definitive identification of the guest species is generally lacking. The similarity of the I_c values for the N_2O_5, Cl_2O_7, and SO_3 derivatives (given in Table IV) with the I_c values for the acid anion relatives in Table III, is striking. Since the familiar forms of the oxides themselves have geometries related to the anions, it is of course possible that much of the intercalant, in all cases, is merely the neutral species. It does seem likely, however, that at least some electron-oxidation of the graphite and guest anion formation has occured, to provide the driving force for the intercalation. This is plausible for the

N_2O_5 and Cl_2O_7, for which oxidation by the following reactions[67] might occur:

$$N_2O_{5(g)} + e^- \text{ (from C)} \rightarrow NO_{2(g)} + NO_{3(g)}^-; \quad \Delta H^\circ \simeq -76 \text{ kcal mole}^{-1}$$

$$Cl_2O_{7(g)} + e^- \text{ (from C)} \rightarrow (ClO_3)_{(g)} + ClO_{4(g)}^-; \quad \Delta H^\circ \simeq -159 \text{ kcal mole}^{-1}$$

The case for SO_3 oxidation of the graphite is less compelling but the possibility of the intercalation being initiated by some polymeric anion formation is great. A general equation for such a reaction is:

$$(x + 3)SO_3 + 2e^- \text{ (from C)} \rightarrow O_3S{\cdot}O{\cdot}(SO_3)_x{\cdot}O{\cdot}SO_3^{2-} + SO_2$$

Some high oxidation-state transition metal oxides (e.g. CrO_3) have also been reported to intercalate. Electron oxidation of the graphite seems to be involved[68].

C. Intercalation of Hexafluoroanions, Fluorine and Arsenic Pentafluoride into Graphite

High carbon-layer charges have been produced with the intercalation of hexafluoroanion species such as MF_6^- (M = P, As, Sb, Os, Ir) and $M'F_6^{2-}$ (M' = Ge, Sn, and Pt) the limiting formulations being, respectively, $C_8^+MF_6^-$ and $C_{12}^{2+}M'F_6^{2-}$. All these salts are blue. Studies involving the third-transition series hexafluorides have demonstrated [64] that a hexafluoride must have an electron affinity of at least 108 kcal $mole^{-1}$ if it is to spontaneously and oxidatively intercalate into pristine graphite.

Data for the third-transition-series haxafluorides and relatives, are given in Table V. Since the haxafluorides are very similar in size [69] the coulomb energy for any salt $C_x^+MF_6^-$ will be essentially the same for all M. In a Born-Haber cycle comparison of the salts $C_x^+MF_6^-$, the only term affecting the enthalpy of formation which changes much, from one salt to another, is the electron affinity of MF_6. The inability of WF_6 + ReF_6 to oxidize and intercalate graphite can be attributed to the lower electron affinities of these molecules. (ReF_7 does intercalate, and WF_6 and ReF_6 each intercalate in the presence of fluorine to yield MF_7^- salts.) Magnetic susceptibility measurements have shown that the limiting-compositions of the osmium, iridium and platinum salts are, respectively, $C_8^+OsF_6^-$, $C_8^+IrF_6^-$, and $C_{12}^{2+}PtF_6^{2-}$.

The essentially close packing of the hexafluorospecies, in the galleries of the C_8MF_6 cases, is required by the unit cell which is illustrated in Figure 8(a). It is probable that the less close-

packed situation pertaining in $C_{12}PtF_6$ (see Fig. 8(b)) is a consequence of the combination of the greater work function required to produce C_{12}^+ (as compared with C_8^+) and the considerable repulsive interaction of the PtF_6^{2-} ions in a close-packed configuration. Note (Figure 8(c)) that each species has six nearest neighbors in a C_8MF_6 - type close-packed configuration, but only three in an ordered $C_{12}MF_6$ arrangement.

The first stage materials are obtained, at $\approx 20^{\circ}$, using the hexafluoride at vapor pressures close to 100 Torr. Higher stages may be obtained by using lower pressures or temperatures. The first stage composition ranges from C_{12} to C_8MF_6. The staging formula for the highest stages is, however, $C_{12n}MF_6$. This is probably a consequence of the large repulsive interactions which the close-packed $C_{8n}MF_6$ formulation requires (see Figs. 8(b), (c)). It appears then that the energy expended in opening another gallery is less than would be lost in adopting a $C_{8n}MF_6$ packing rather than a $C_{12n}MF_6$ packing. In the former each anion would have six nearest neighbors, whereas in $C_{12n}MF_6$ there are three near neighbors only.

The first stage osmium and iridium compounds do not conduct electricity [78], in the ab plane , much better than graphite itself. This is also the case for the platinum compound, even in the second stage. On the other hand for the second and higher stages, derived from OsF_6 or IrF_6, the σ_{ab} values are approximately an order of magnitude greater than for graphite itself. Bartlett et. al. [64] have pointed out that the lower conductivity in the more highly charged graphites may be a consequence of distortion of the carbon layers. They note eventual loss of crystallinity in $C_8^+MF_6^-$ (M = As, Os, Ir). When freshly prepared and kept at low temperatures

these salts exhibit the diffraction characteristics required for the cell given in Fig. 8(a), but at room temperature the crystallinity is lost within a few hours. The salts C_8MF_6 (M = P or As) can be made [79, 80] by treating graphite with a mixture of the pentafluoride and fluorine until there is no further consumption of either gas. The arsenic salt conductivity is comparable with that of graphite, in contrast with the graphite-arsenic pentafluoride relative, C_8AsF_5, which is comparable with aluminum metal [78, 81, 82].

It is not possible to intercalate, BF_3 or PF_5 or WF_6 alone into pristine graphite. Evidently, as Lewis acids, their interaction with graphite Π clouds cannot provide for the energy of the gallery opening. The data in Table VI show, however, that the fluoride-ion affinities of each of these molecules is large. This enthalpy evidently drives the intercalation of the ions derived from them.

Munch et. al. [95] and McCarron et. al. [80] have independently noted that the consumption of fluorine by graphite in the presence of arsenic pentafluoride is double that required to form AsF_6^-. Bartlett and his coworkers [78, 80, 96] have shown that for stages $n \geq 2$, the limiting composition of these fluorine-rich systems is $C_{12n}AsF_6.F$. The fluorine cannot be removed under vacuum but it can be titrated with AsF_3, to form an AsF_6^- salt:

$$3C_{4y}AsF_6.F + AsF_3 \longrightarrow 4C_{3y}AsF_6$$

and with an equimolar quantity of AsF_3 there is complete conversion to a material which appears to be identical to that prepared directly from graphite and AsF_5. The interaction is evidently:

$$2C_{3y}AsF_6.F + AsF_3 \longrightarrow 3C_{2y}AsF_5.$$

The extra fluorine for the $C_{12n}AsF_6.F$ occupies only those galleries which contain AsF_6^-. It seems likely that the fluorine, as F^-, is located in the vacancies available in the $C_{12}AsF_6$ gallery. Since each of these vacancies (see Figure 8 (b), (c)) can accomodate an AsF_6^- (as in C_8AsF_6) the requirement that each accomodate two F^- is easily met. Of course this means that the positive charge in the carbon layers in these fluorine-rich compounds must be high, viz: $C_{12n}^{2+}AsF_6^-.F^-$.

Thompson et.al. [78] have found that the $C_{12n}AsF_6.F$ materials are poor ab plane conductors and that their reduction by AsF_3 leads to conductivity enhancement. This low conductivity of $C_{12n}^{2+}AsF_6^-.F^-$ parallels the low conductivity noted for the first stage $C_8^+MF_6$ salts and those derived from PtF_6^{2-}.

These discoveries are pertinent to the long standing problem of the non intercalation of elemental fluorine in pristine graphite [3, 9]. It is clear that fluorine is unable (unaided) to open a gallery and this continues to be the case for $C_{12}AsF_6$, which will only take up fluorine ($C_{12}AsF_6 + \frac{1}{2}F_2 \longrightarrow C_{12}AsF_6.F$) within the occupied gallery. Perhaps (to follow a suggestion of Hooley [9]), F^- formed at the opening to a gallery, become fixed at the entrance and cannot move forward into the gallery. Such localization of F^- is compatible with their small size (radius 1.33A) and large charge density [97]. Once close to a somewhat positively charged carbon atom, the progression to another carbon (at least 1.42Å distant) requires appreciable energy.

It may be that, with the AsF_6^- in attendance, the progression into the occupied galleries is aided by the fleeting formation of specied such as AsF_7^{2-}, or even AsF_7^-. Such species, with their

overcrowded coordination spheres would slough off a ligand readily, but the one discarded need not be the one taken up. By such a ligand exchange the F^- could progress rapidly into (and out of) the gallery. But there is presently no evidence to give firm support to such conjectures.

Perhaps the materials which have aroused most interest and controversy are those derived from graphite and AsF_5. Selig and his coworkers [98] were the first to report such a material but it was the report of conductivities comparable with that of copper [81] which attracted much attention. More recent work indicates that the conductivities are lower than first assessed, but values comparable with aluminum metal are established [78, 82].

Most of the controversy has centred on the nature of the guests. Bartlett et. al. [20, 21] have contended, on the basis of X-ray absorption edge studies, that the arsenic pentafluoride oxidizes the graphite according to the equation:

$$3AsF_5 + 2e^- \longrightarrow 2AsF_6^- + AsF_3$$

and that the conversion to AsF_6^- and AsF_3 is virtually complete. They have also shown that there are substantial fractions of arsenic trifluoride present in the volatiles removed from the intercalated graphite [80]. Moreover, they have shown [78] that when AsF_3 is added to a $C_{12n}AsF_6$ salt ($n \geqslant 2$), there is no detectable change in stage and the conductivity remains unchanged. The same holds for removal of AsF_3. These observation are in accord with a $C_{12n}AsF_6$ structure (see Figure 8(b)) into the vacancies of which can be placed neutral AsF_3 molecules, to yield a material $C_{12n}AsF_6 \cdot \frac{1}{2}AsF_3$ (i.e. $C_{8n}AsF_5$). A persuasive feature is that the staging formula for graphite/ AsF_5 [99]

is $C_{8n}AsF_5$ (i.e. $C_{12n}AsF_6 \cdot \frac{1}{2}AsF_3$) whereas for the AsF_6^- salts it is $C_{12n}AsF_6$ [80].

The thermodynamic data in Table VII, when taken in conjunction with that in Table V, indicate that AsF_5 (and SbF_5) should be capable of oxidizing graphite, since the electron affinity, per equivalent of electron oxidation of the graphite, is comparable with that of OsF_6. On the other hand, PF_5 has a lower electron affinity (for the reaction $3PF_5 + 2e^- \longrightarrow 2PF_6^- + PF_3$) than does WF_6. It is, therefore, not surprising that PF_5, alone, will not oxidize graphite spontaneously.

In spite of this evidence the early views [100, 101] that the guest species were largely molecular AsF_5 (or AsF_5 bonded to the graphite Π system) have persisted [102]. The major problems appear to be chemical. (Unfortunately many physical measurements have been made on materials which have been ill-defined chemically.)

Although AsF_6^- and AsF_3 are the dominant guest species, nevertheless, they are in equilibrium with AsF_5. The latter becomes a more important species as the charge builds up in the carbon layers (which it does, dramatically, in passing from second to first stage). Thus we have:

$$G + 3AsF_5 \rightleftharpoons G^{2+}2AsF_6^- + AsF_3$$

Indeed if a large excess of arsenic pentafluoride is used in the synthesis, as AsF_3 leaves the material it can be replaced by AsF_5. Hence, unless the preparative conditions are closely specified, it is unlikely that a pure graphite AsF_5 compound will be obtained. The ready loss of AsF_3, means that it is possible to make a graphite AsF_6^-

salt, from graphite and AsF_5, simply by repeating a cycle of operations. Thus, C_8AsF_5 under vacuum passes to $C_{\sim 14}AsF_{5-6}$. The latter is treated with more AsF_5 to a composition C_8AsF_{5-6}, again pumped down and again treated with AsF_5. After five such cycles, the composition stands (after evacuation) close to the first-stage composition $C_{12}AsF_6$ [96].

Although there is no detectable difference between the ab plane conductivities of second and higher stages of $C_{8n}AsF_5$ and $C_{12n}AsF_6$ [78], there are large differences between the first stage materials. C_8AsF_5 is a good conductor (about twelve times better than graphite) whereas $C_{12}AsF_6$ (like $C_{12}MF_6$ (M = Os, Ir)) has a conductivity close to that of graphite itself. There is no evidence of loss of crystallinity in C_8AsF_5 as there is for C_8AsF_6, and it appears that the graphite layers have their hexagonal symmetry preserved in the former.

A somewhat haphazard arrangement of the neutral and charged species (AsF_6^-, AsF_3 and some AsF_5) in the galleries of C_8AsF_5 will mean a lower tendency to charge localization at specific sites in the carbon layer than in $C_8^+AsF_6^-$. Thus the delocalized π electron system of graphite may be less perturbed in C_8AsF_5 than in $C_8^+AsF_6^-$, where a guest on each side of a carbon layer will cooperate to localize positive charge. Such cooperative charge localization could lead to structural change in the carbon layers.

Unfortunately most of the studies on graphite/AsF_5 have been made on materials which must now be regarded as suspect. When close attention is given to the chemical problems, the points of dispute may well disappear.

D. Intercalation of Halogens and Halides (except Fluorides)

Hérold has thoroughly discussed the intercalation of halogens and halides into graphite [3] and has discussed much of the structural work in detail, therefore these aspects will not be treated again here.

From the enthalpies of formation of the halide ion (given in Table VIII), electronegatives, and lattice energetics, the lightest of the halogens are the most favorable for the formation of salts $C_x^+ X^-$ (x=halogen). With the possible exception of F^- in salts such as $C_{12n} AsF_6 \cdot F$ ($n \geq 2$), there is no evidence that discrete halide ions ever occur in intercalation compounds of graphite. Chlorine forms compounds [10⁴] which are stable below room temperature. Bromine is the only halogen which spontaneously generates a graphite compound at ordinary temperatures and pressures. Iodine does not intercalate, yet ICl and IBr do so. Hooley [9] has pointed to the close compatability of the internuclear distances in those molecules which do intercalate: Br_2 (2.27Å); ICl (2.40Å); IBr (2.49Å), with the center to center distance of adjacent hexagons in graphiteof 2.42Å. Perhaps this preserves the electron delocalization of the carbon layers by spreading any positive charge, associated with electron removal by the bromine, more or less evenly over the hexagons of carbon atoms.

There is a further feature of these Br_2, ICl, and IBr molecules, as distinct from F_2 and Cl_2, which may contribute to their ease of intercalation into graphite: that is their readiness to bond to related species to form extended halogen-bridged systems [105]. Thus Br_3^-, Br_5^- and even more extended species may have a role in bromine intercalation. Similarly, ICl_2^-, IBr_2^- or $I_2Cl_3^-$ and $I_2Br_3^-$ may contribute to the intercalation of ICl and IBr. In all of these simple halogen and interhalogen intercalation compounds, the physical evidence points clearly to a small charge transfer per halogen atom. It is clear that the transfer of one electron brings about the intercalation of many halogen atoms. The bridging ability of the heavier halogens may well be a crucial component to this intercalating capability. But that capability alone cannot be sufficient since iodine forms such extended systems (e.g. I_3^-, I_5^-, I_7^-) with ease and with appreciable energy benefit. It seems that, in comparison with the other halogens, because of its larger size (and the resultant poor lattice energy), low electronegativity, and poorer energy of anion formation, iodine is unable to meet the energy requirements for opening a gallery in graphite.

Although a large number of halides have been reported to intercalate into graphite, many of these are high-oxidation-state metal halides which are recognized as strong Lewis acids (e.g. $SbCl_5$, $NbCl_5$). Except for species such as $AuCl_4^-$, which

prefer a square planar geometry [106], the I_c values (e.g. 9.5Å for chlorides) indicate that the gallery contains a double layer of halogen ligands.

In a number of cases arguments have been advanced that the guest species have much the same geometry as in the pure guest precursor [3]. If this is so, the reason for intercalation is not evident. It seems likely that in most, if not all, of such halide intercalations, that anion formation may be a necessary energy-providing step. The anion may be a very large, halogen-bridged species bearing small charge on a per-halogen basis.

The clearest indication that anions can be important, is associated with the intercalation of the Al, Ga, and In chlorides and bromides. These halides intercalate into graphite only in the presence of excess halogen. The data for the Al and Ga compounds in Table VIII show that the formation of the simple MX_4^- (g) species, is, in each case, highly energetically favorable for larger species $(MX_3)_n X^-$, the energy liberated, per mole of electrons taken up in forming the anion, is probably comparable to the MX_4^- case. Of course, the larger the anion, the smaller is the lattice energy but then the number of electrons to be removed from the carbon layers, for each mole of 'MX_3' is also less.

It will be realized that species such as MX_3 (M= Al, Ga; X= Cl, Br) can only provide halogen for $(MX_3)_n X^-$ production by reduction to a lower halide. Such reduction is energetically

unfavorable for these halides. This may not be the case for most of the higher-oxidation-state transition metal halides. Ferric chloride may be such a case.

In spite of the considerable attention given to the graphite $FeCl_3$ system, it is not yet certain what the guest species are. It is clear from Mossbauer studies [109] that the iron is all Fe III. Electron excitation studies [110] have also shown that one electron is transferred from the carbon layers for approximately ten iron atoms intercacated. This implies that there must be one extra chlorine (chloride) for every ten $FeCl_3$ molecules intercalated. Analytical data is scarce and there is not explicit claim for a first-stage $C_x Fe_{10} Cl_{31}$ stoichiometry as far as the present reviewers are aware. The thermodynamic data in Table VIII do lend support to the hypothesis that reduction of some $FeCl_3$ to $FeCl_2$ could provide the halogen for the intercalation of a complex $(FeCl_3)_n Cl^-$ guest. The $FeCl_2$ would presumably remain external to the graphite. Comparable redox schemes are also plausible for many of the other metal halides which are reported to intercalate spontaneously into graphite.

Stumpp and his co-workers have succeeded in preparing a large number of graphite intercalation compounds from transport of those halides by forming complexes with $AlCl_3$ [114]. Schaeffer has given a comprehensive survey [113] of the thermodynamic features which form the basis of this vapor transport. Stumpp has noted that, in many instances, intercalation of the metal halide will only occur in the presence of free halogen. Again,

it seems that at least some guest-anion formation provides the energetic basis for the intercalation

VI. INTERCALATION WITHOUT APPARENT OXIDATION OR REDUCTION OF THE GRAPHITE

In many cases the assumption has been made that the guests within graphite galleries are uncharged. This is unlikely to be so in the majority of cases but, there are a number of cases where spontaneous intercalation of the graphite does not appear to involve oxidation or reduction.

A set of compounds which are in this catagory are the noble-gas fluorides. Although these are powerful oxidizers, it appears to be unlikely that they electron-oxidize graphite. Thus krypton difluoride intercalates spontaneously and appears to have an enhanced stability when intercalated. The graphite KrF_2 material is also a less extreme fluorinating and oxidizing agent than KrF_2 itself. Yet, reduced species such as KrF_2^- cannot be formed. Nor are species such as KrF_3^- very probable. It appears that KrF_2 must be present as the molecular species.

A related set of compounds which appear to behave similarly to the noble-gas fluorides are halogen fluorides. Those which intercalate spontaneously include BrF_3, IF_5 and IOF_5. Most of the work on these fluorides and the noble-gas fluorides was initiated by Selig and his co-workers and a full report of the chemical and analytical aspects of their intriguing graphite intercalation compounds are given in the comprehensive review by Selig and Ebert [5].

It is perhaps relevant that in both the noble-gas fluorides and the halogen fluorides, semi-ionic bonding [117] occurs. Thus KrF_2 can be represented as a resonance hybrid of the canonical

forms $(FKr)^+ F^-$ and $F^-(KrF)^+$. Similarly BrF_3 can be represented as the resonance hybrid of the canonical forms $(F\ Br(F))^+ F^-$ and $F^-(Br(F)F)^+$. These semi-ionic bonds bestow large multipole moments on these molecules. It is likely that they produce appreciable π cloud perturbation in the carbon-layers which result in appreciable multipole-multipole attraction between guest and host. Further insight must clearly await more detailled structural studies than have appeared so far.

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91. Values for P and As species are for the gas phase wheras for Sb equation (1) represents conversion of polymeric liquid SbF_5 and equation (2) the conversion of liquid SbF_5 into solid SbF_3. Since the heat of vaporization and the enthalpy of formation of the gaseous monomer, $SbF_{5(g)}$, are both endothermic, the enthalpy change for equation (3) in the Sb case must be more exothermic than given here.

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Table I Gallery height data for graphite compounds of the more electropositive metals

Compound	Stage	Color	Occupied gallery height I_c (Å)	$I_c - 3.35$* (Å)	Metal-ion** diam. (Å)
C_8K	1	gold	5.41	2.06	K^+, 3.02
$C_{24}K$	2	blue	8.77	2.07	
$C_{36}K$	3	blue	12.12	2.07	
$C_{48}K$	4	blue	15.49	2.09	
C_8Rb	1	gold	5.65	2.30	Rb^+ 3.32
$C_{24}Rb$	2	blue	8.97	2.27	
C_8Cs	1	gold	5.94	2.59	Cs^+ 3.62
$C_{24}Cs$	2	blue	9.25	2.55	
C_6Li	1	brass yellow	3.73	0.38	Li^+ 1.80
C_6Ca	1	pale yellow	4.55	1.20	Ca^+ 2.28
C_6Sr	1	yellow	4.95	1.60	Sr^{2+} 2.64
C_6Ba	1	yellow	5.25	1.90	Ba^{2+} 3.00
C_6Eu	1	yellow	4.85	1.50	Eu^{2+} 2.61 Eu_{2+} 2.17
C_6Sm	1	yellow	4.72	1.37	Sm^{2+} 2.72 Sm_{2+} 2.20
C_6Tm	1	yellow	4.62	1.27	Tm^{2+} 2.34 Tm_{2+} 2.04
C_6Yb	1	gold	4.57	1.22	Yb^{2+} 2.36 Yb^{2+} 2.02

* The metal species nestle in the dimples of the carbon layers hence Ic-3.35A should be less than the species diameter.

** R. D. Shannon Acta Cryst., A32, 751, 1976.

Table II Basal Plane Conductivities for some Alkali Metal-Graphite Compounds *

Compound stage (n)	Alkali	** t/t_o	$\sigma_o(10^4\ \Omega^{-1}\text{-cm}^{-1})$	*** $\sigma_o t/t_o(10^4\ \Omega^{-1}\text{-cm}^{-1})$
1	C_8K	1.62	11 9	18 15
2	$C_{24}K$	1.31	12	15
3	$C_{36}K$	1.21	17	20
1	C_8Rb	1.69	8	14
2	$C_{24}Rb$	1.34	-	-
3	$C_{36}Rb$	1.23	15	18
4	$C_{48}Rb$	1.17	19	22
1	C_8Cs	1.77	11 8	20 15
2	$C_{24}Cs$	1.39	12	16
3	$C_{36}Cs$	1.26	-	-
4	$C_{48}Cs$	1.19	14	17

* reference 51.

** t/t_o = ideal c axis expansion from the formula $t/t_o = \frac{3.35(n-1)+I_c}{3.35n}$

*** σ_o normalized to account for thickness t_o having the same number of carbon layers as thickness t.

Table III. Intercalated-gallery spacings for some strong-acid salts.

first-stage formula *	$C_8H_pSO_4$	C_7SO_3F	$C_7H_tSO_3F$	$C_8H_tClO_4$	$C_{4.3}H_xNO_3$
reference	[59]	[65]	[65]	[59]	[59]
I_c(Å)	7.98	7.73	8.01	7.85	7.8

* $p \simeq 1 + 2/3$; $t \simeq 2/3$; $x \simeq 5/6$

Table IV. Intercalated-gallery spacings for some compounds with oxides.

reagent	SO_3	Cl_2O_7	N_2O_5
reference	[3]	[3]	[63]
graphite compound formula	$C_{5n}SO_3$	$C_{12n}Cl_2O_7$	$C_{8n}N_2O_5$
stages	1,2,3	1,2,3	2,3,4
I_c (Å)	7.96-7.90	7.92-7.80	7.8

Table V. Electron Affinties, A (kcal mole^{-1}), of Third Transition Series Hexfluorides and their Graphite-Salt Limiting Compositions

WF_6	ReF_6	OsF_6	IrF_6	PtF_6
81[d]	107[a]	135[a]	161[a]	188[a]
-	-	$C_8^+OsF_6^-$[e,f]	$C_8^+IrF_6^-$[e]	$C_{12}^{++}PtF_6^{--}$[e]
	MoF_6	UF_6		
	117[b]	113[a]		
	C_8MoF_6[c]	C_9UF_6[j]		

(a) The oxidative chemistry of the third transition series hexafluorides had established a smooth increase in oxidizing capability from W to Pt and Bartlett [69] had estimated that the electron affinity increases by $\sim$1 eV for each unit increase in atomic number across the series. There has, however, been much uncertainty about the absolute values of the electron affinities A(MF_6), some of this uncertainty springing from uncertainties in evaluations of lattice energies for salts, such as $NO^+MF_6^-$ and $O_2^+PtF_6^-$. Here, we have, for the first time, tied A(MF_6) to A(UF_6). Two independent measurements for A(UF_6) give 113 [70] and 117 [71] kcal mole^{-1}. The former value derives from ion-cyclotron resonance studies, from which studies a

Table V cont'd

rather precise value is also available for $A(WF_6)$, hence we take it as our fixed point for $A(UF_6)$. Calorimetric studies [72] give $\Delta H°(NO(g) + UF_{6(g)} \longrightarrow NO^+UF_{6(c)}^-) = -52$ kcal mole^{-1}. Since the first ionizatin potential, I(NO), is 213 cal mole^{-1}, and $A(UF_6) = 113$ kcal mole^{-1}, it follows that the lattice energy $U(NO^+UF_{6(c)}^-) = -152$ kcal mole^{-1}. A similar calorimetric study [73] has given $\Delta H°(O_{2(g)} + PtF_{6(g)} \longrightarrow O_2^+PtF_{6(c)}^-) = -60$ kcal mole^{-1}. Therefore, because $U(O_2^+PtF_{6(c)}^-)$ must be slightly more exothermic than $U(NO^+UF_{6(c)}^-)$, since PtF_6^- is smaller than UF_6^-, the electron affinity of PtF_6 must be slightly greater than $I(O_2) + U(NO^+UF_{6(c)}^-) - \Delta H°(O_{2(g)} + PtF_{6(g)} \rightarrow O_2^+PtF_{6(c)}^-) = (278 - 152 + 60)$ kcal mole^{-1}. Accordingly we set the electron affinity of PtF_6 at 188 kcal mole^{-1}. Since $A(WF_6)$, derived from ion-cyclotron resonance studies [74], is in harmony with less precise evaluations [69] from other experiments, and is also compatible with the known oxidative chemistry of WF_6, we accept this value as our other fixed point for the third transition series. The estimates of $A(MF_6)$ for PtF_6, OsF_6 and IrF_6 have been derived, assuming a smooth increase with atomic number of M, between $A(WF_6) = 81$ kcal and $A(PtF_6) = 188$ kcal mole^{-1}. Although the lattice energy $U(O_2^+PtF_{6(c)}^-) = -154$ kcal^{-1} is higher than that derived from a Kapustinskii lattice energy, the $A(MF_6)$ based on the higher lattice energy are in excellent agreement with the known oxidative chemistry. (b) ref 75 (c) ref 76 (d) ref 74 (e) ref 64 (f) ref 20 (g) ref 77

Table VI. Enthalpy changes for the formation of some fluoroanions:

$$\Delta H(MF_{x(g)} + 1/2F_{2(g)} \longrightarrow MF_{(x+1)(g)}^{-})\ [83]$$

MF_x	BF_3	PF_5	AsF_5	SbF_5	WF_6
ΔH(kcal mole^{-1})	-155	-158	-170	-193	-141
references	86	87,88	87,20	87,89	90

Table VII. Enthalpy changes for electron-oxidation by Group V pentafluorides [91] (values in kcal mole^{-1})

		P	As	Sb
(1)	$\Delta H°(2MF_{5(g)} + F_2 + 2e^- \rightarrow 2MF_{6(g)}^-)$[a]	$\leq$ -316	$\leq$ -340	-386
(2)	$\Delta H°(MF_{5(g)} \rightarrow MF_{3(g)} + F_{2(g)})$	152[b]	98[c]	90[d]
(3)	$\Delta H°(3MF_{5(g)} + 2e^- \rightarrow 2MF_{6(g)}^- + MF_{3(g)})$	$\leq$ -164	$\leq$ -242	$\leq$ -296
	Electron affinity (according to eqn. (3))	$\geq$ 82	$\geq$ 121	$\geq$ 148

(a) See Table VI; (b) ref. 92; (c) ref. 93; (d) ref. 94

Table VIII. Some enthalpies of formation for halide and complex halide ions (kcal $mole^{-1}$) [a]

	X:	F	Cl	Br	I
ΔH_f° ($X_{2(g)} + e^- \rightarrow X^-_{(g)}$) :		-64	-57	-58	-56

	Al	Ga
ΔH° ($\frac{1}{2}M_2Cl_{6(g)} + \frac{1}{2}Cl_2 + e^- \rightarrow MCl_4^-{}_{(g)}$)	-128 [b]	-133 [b]
Reported limiting compositions of graphite compounds	$C_9AlCl_{3.5}$ [c]	$C_9GaCl_{3,5}$ [d]
H ($MBr_{3(g)} + \frac{1}{2}Br_2 + e^- \rightarrow FeCl_4^-{}_{(g)}$)	-133 [b]	-128 [b]

	Fe [e]
$\Delta H(FeCl_{3(g)} + \frac{1}{2}Cl_2 + e^- \rightarrow FeCl_4^-{}_{(g)})$	-161
$\Delta H(FeCl_{3(g)} \rightarrow FeCl_{2(c)} + \frac{1}{2}Cl_2)$	+22
$\Delta H(2FeCl_{3(g)} \rightarrow FeCl_{2(c)} + FeCl_4^-{}_{(g)})$	-139

a: ref.103; b: ref.107; c: ref.108; d: ref.109;

e: Calculated from the enthalpies of reaction of $KCl_{(c)}$ or $NaCl_{(c)}$ with $FeCl_{3(c)}$ to make $KFeCl_{4(c)}$ and $NaFeCl_{4(c)}$ [112], the lattice energy of NaCl [113], and a Kapustinskii radius of 3.58A [114]. If the radius is lowered to 3.18A the lattice eenergy is increased and the chloride ion affinity of $FeCl_{3(g)}$ is decreased by 13 kcal $mole^{-1}$.

FIGURES

1. Staging in graphite intercalation compounds.
2. (a) Fragment of a graphite layer and (b) layer-layer registry in different graphites.

3(a) The unit cell and first and second Brillouin zones for a single graphite layer. (The first Brillouin zone is a hexagon whose sides are distant $1/\sqrt{3}a$, from its center. Only at each point of this hexagon is there zero energy gap with the second Brillouin zone.)

3(b) Electron energy levels (at 0°K) in a single graphite carbon layer, in pristine, reduced, and oxidized condition.

4. The domain model for graphite staging: (a) staging (b) interaction of elastic dipoles.
5. Unit cells for ordered C_6M' and C_8M intercalation compounds. (with guest species in sites $\underline{\alpha}$ in one gallery those in succeeding galleries may, or may not, be in sites β, γ or δ).
6. Alternative packing arrangements for (a) tetrahedral species (b) planar NO_3 species.
7. Projection into (001) plane of a $C_{24}{}^{+}HSO_4{}^{-}2H_2SO_4$ structural modification (after Rudorff 59). The full $\underline{c}$ axis sequence of guest layers is 1,2,3,1,3,2,1.
8. Ordered structural arrangements for (a) C_8MF_6 (b) $C_{12}MF_6$ and (c) appropriate close-packing of guest models for (a) and (b).

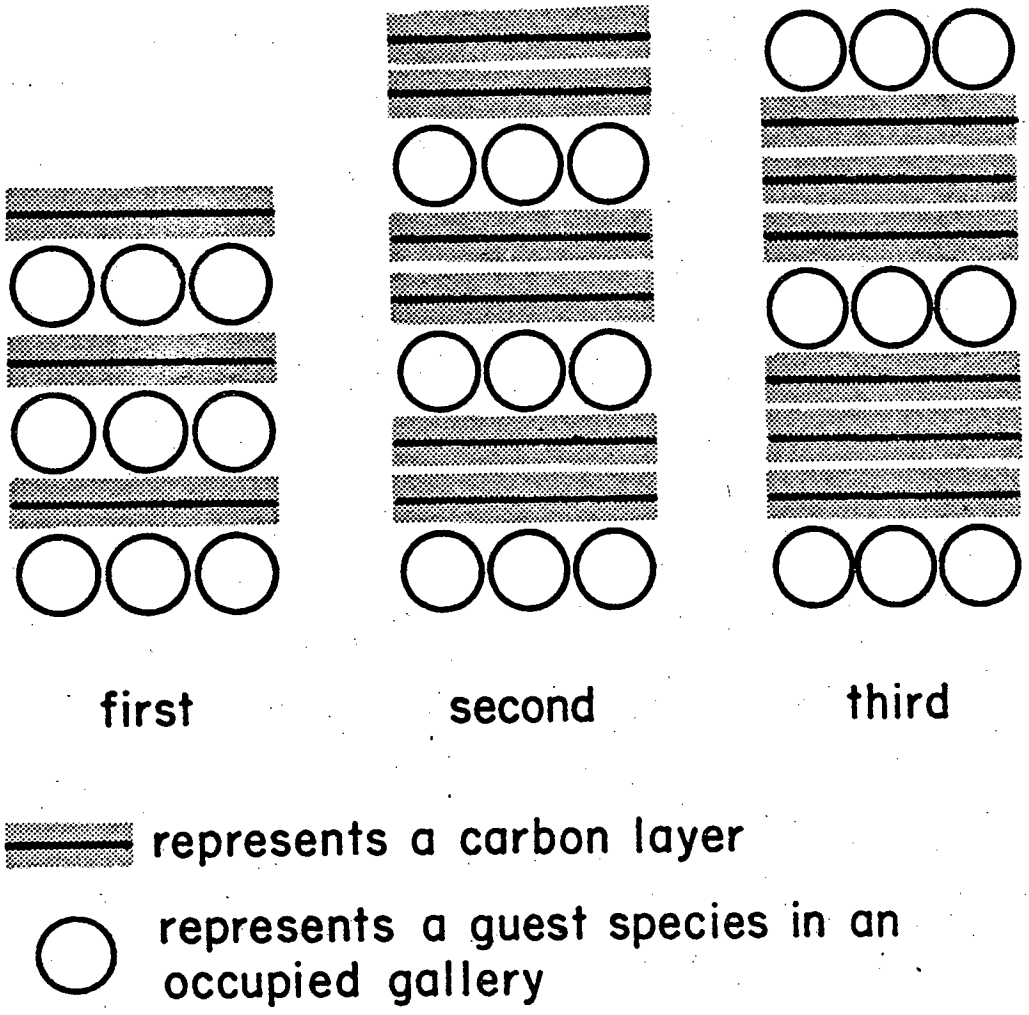


Figure 1. Staging in graphite intercalation compounds.

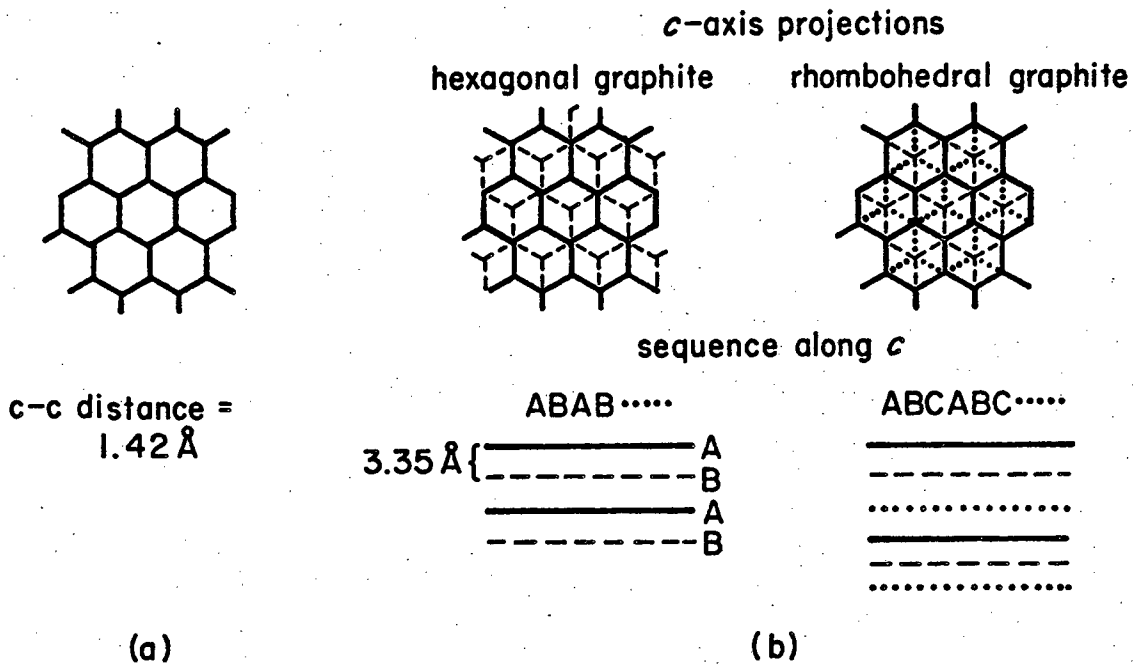
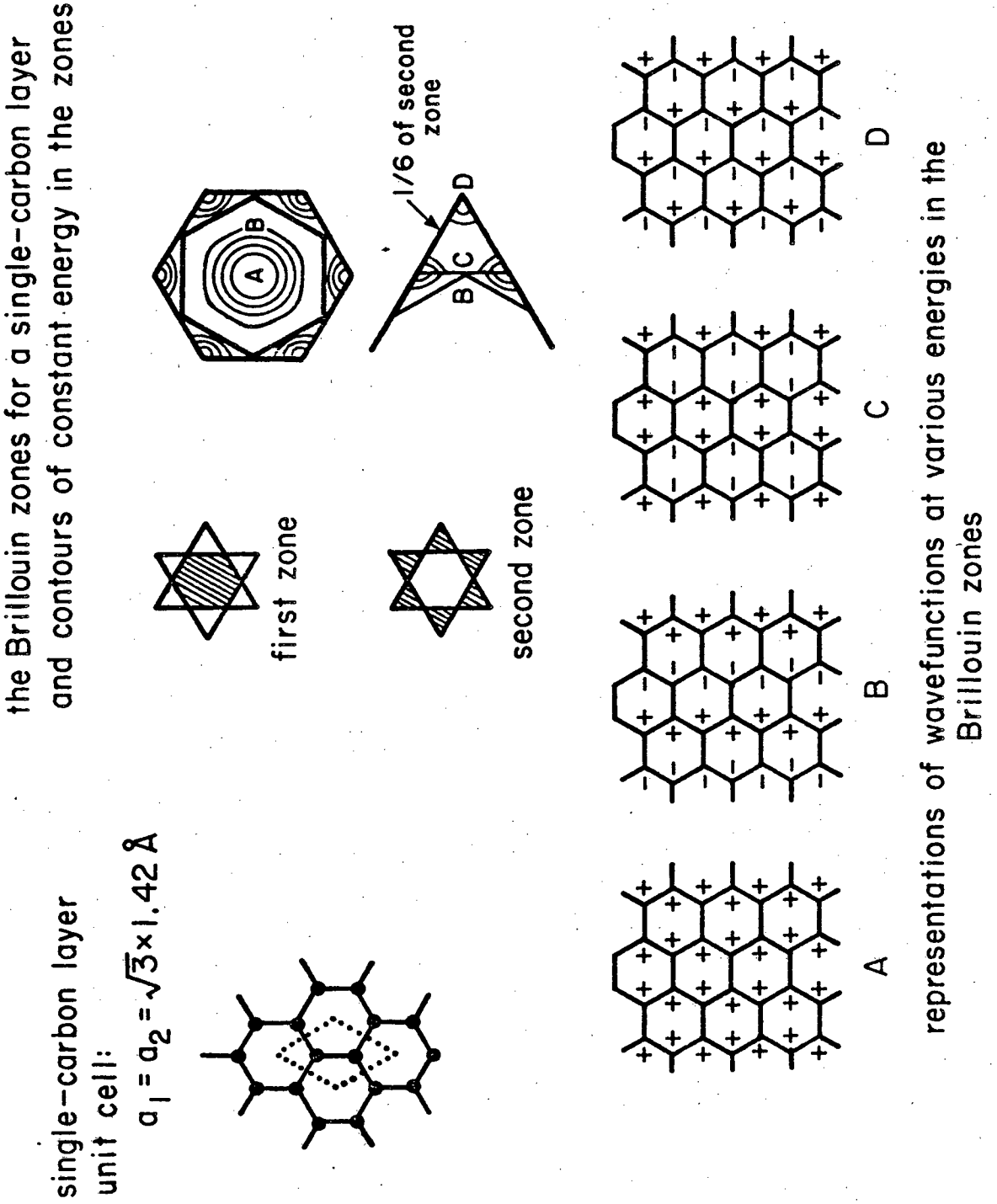


Figure 2. (a) Fragment of a graphite layer and (b) layer-layer registry in different graphites.



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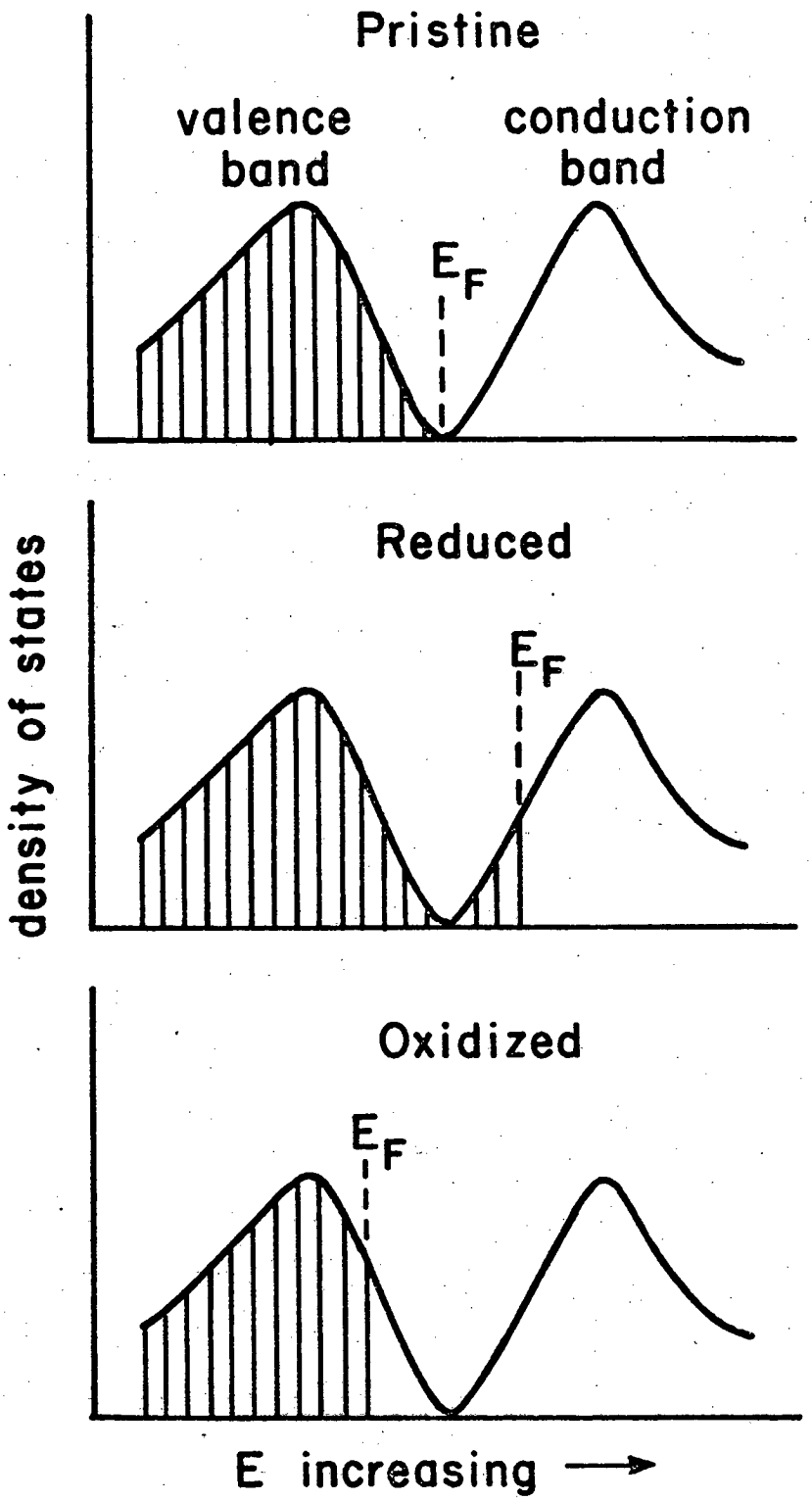

Figure 3(b). Electron energy levels (at 0°K) in a single graphite carbon layer, in pristine, reduced, and oxidized condition.

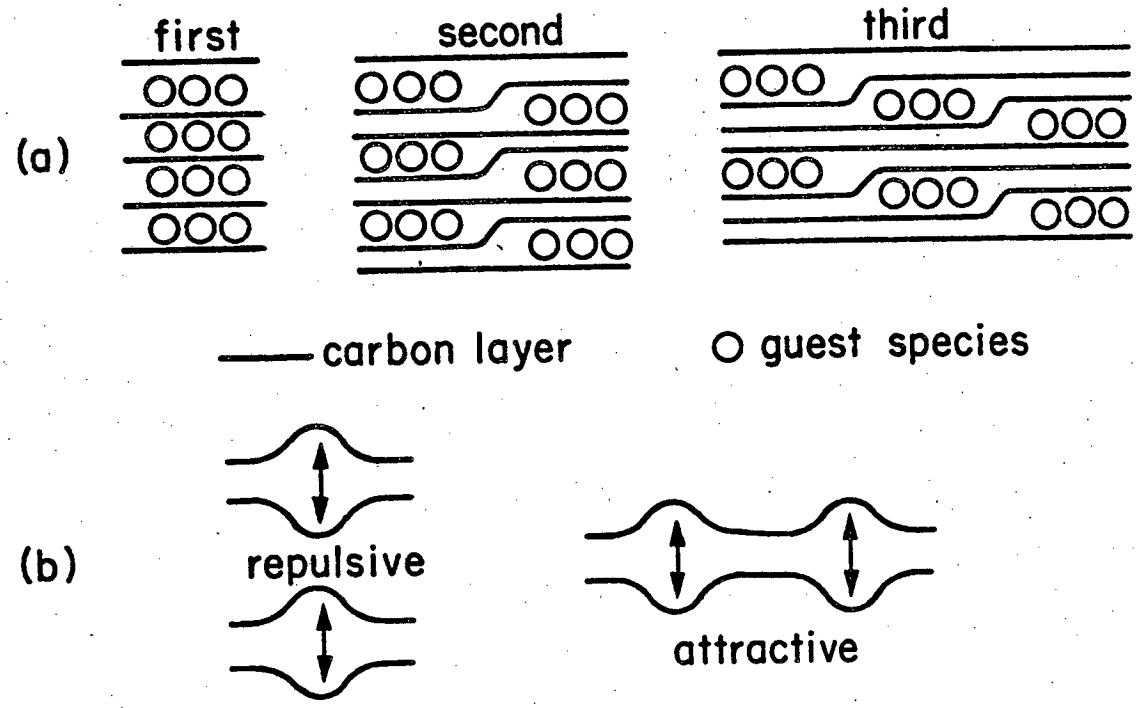

Figure 4. The domain model for graphite staging: (a) staging (b) interaction of elastic dipoles.

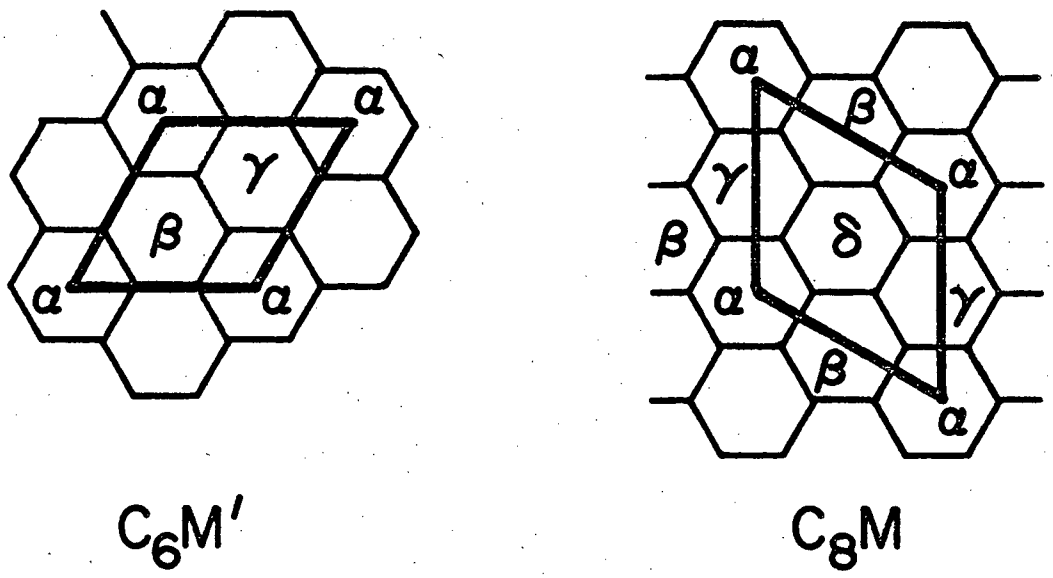

Figure 5. Unit cells for ordered C_6M' and C_8M intercalation compounds. (with guest species in sites $\underline{\alpha}$ in one gallery those in succeeding galleries may, or may not, be in sites β, γ or δ).

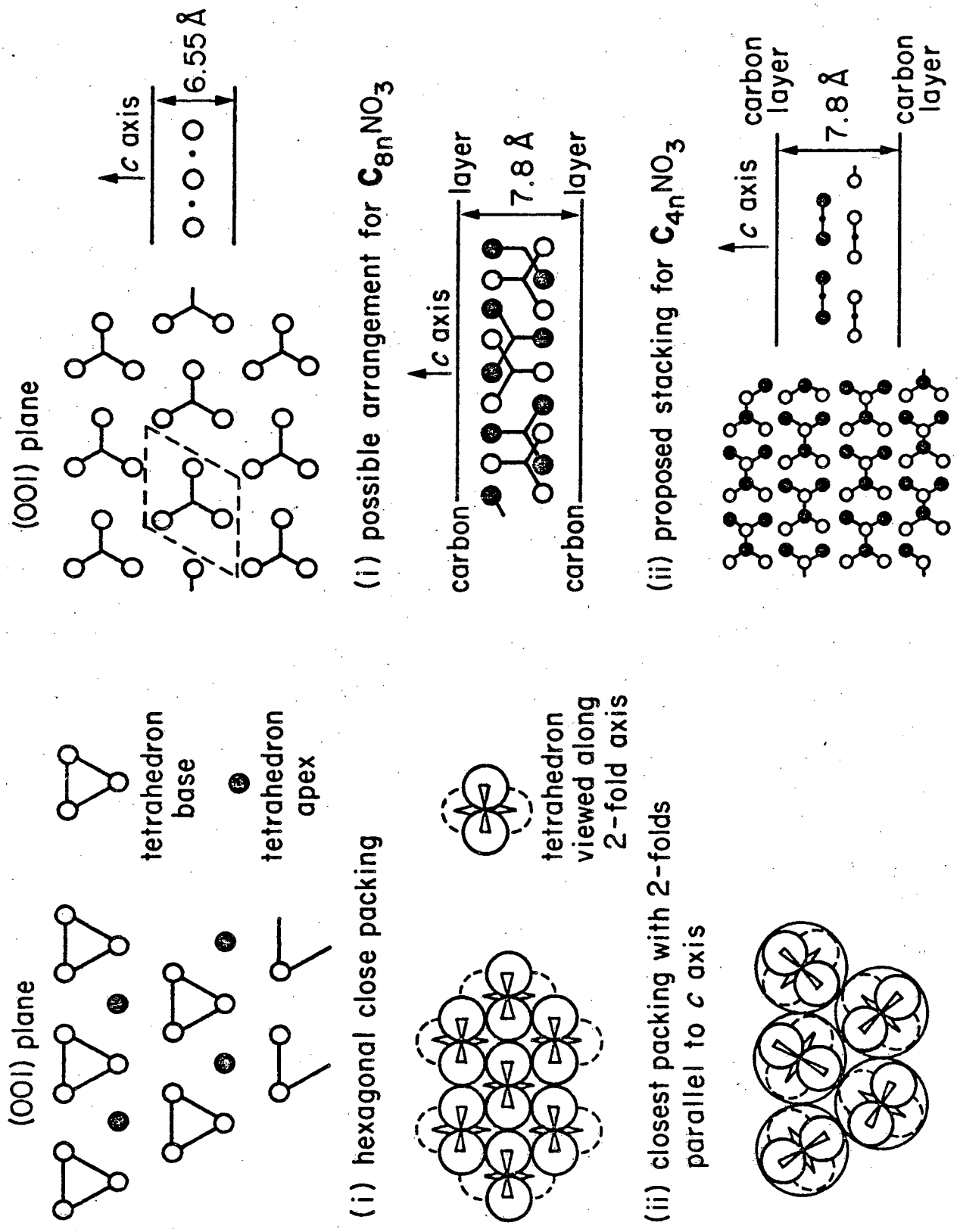

Figure 6. Alternative packing arrangements for (a) tetrahedral species (b) planar NO_3 species.

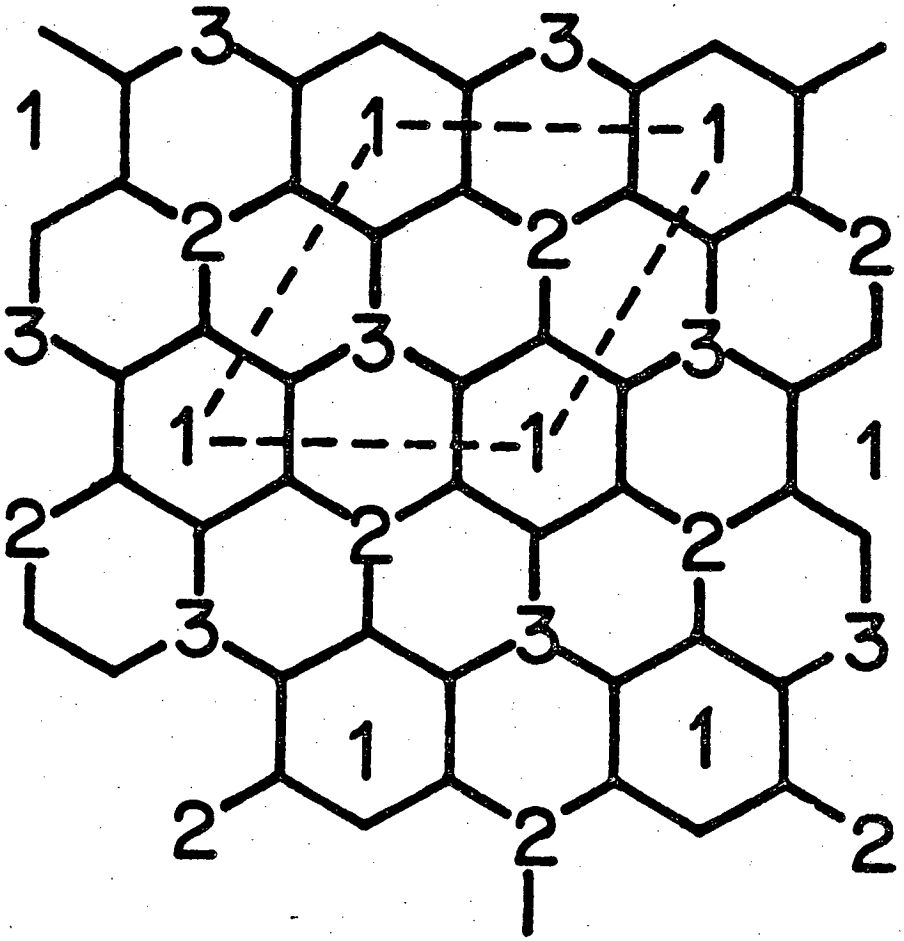

Figure 7. Projection into (001) plane of a $C_{24}^{+}HSO_4^{-}2H_2SO_4$ structural modification (after Rudorff 59). The full c axis sequence of guest layers is 1,2,3,1,3,2,1.

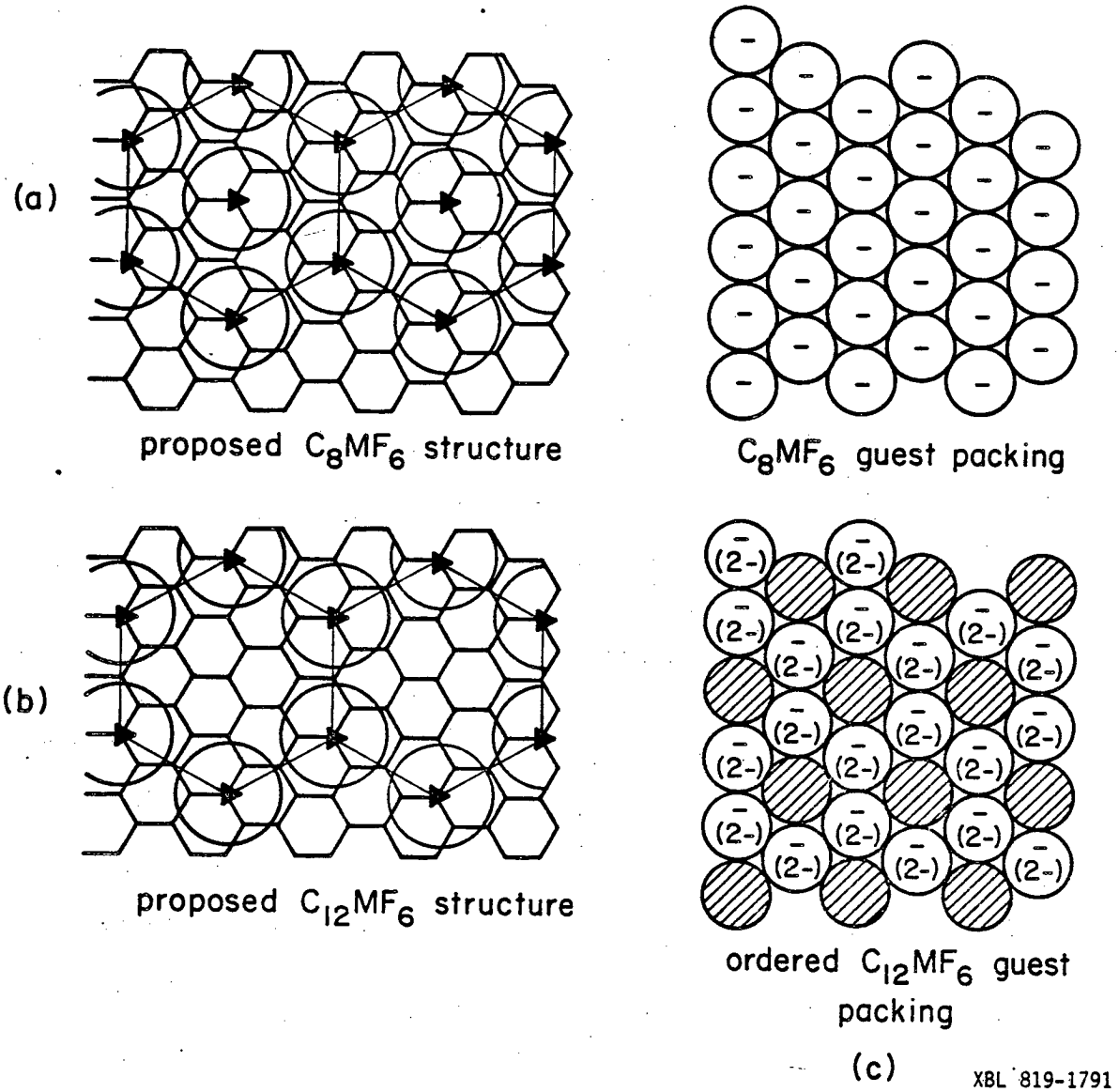

Figure 8. Ordered structural arrangements for (a) C_8MF_6 (b) $C_{12}MF_6$ and (c) appropriate close-packing of guest models for (a) and (b).

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