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ON THE ROLE OF INORGANIC FLUORINE CHEMISTRY IN THE STUDY OF SYNTHETIC METALS*

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SUMMARY

The intercalation of metal hexafluorides (MF_6) into graphite proceeds according to the reaction

$$nC + MF_6 \rightarrow C_n^{+x}(MF_6^-)_x(MF_6)_{1-x}$$

where x is the degree of charge transfer. The latter can be determined by magnetic measurements. It varies approximately linearly with the electron affinity of the MF_6.

The doping of polyacetylene by MF_6 is believed to proceed by a similar reaction.

In recent years there have been remarkable developments in a new field called 'Synthetic Metals.' By synthetic metals we refer to materials having some properties common to metals such as high electrical conductivity and light reflectivity, but which are composed of materials other than the classic metals. Among the important classes of synthetic metals are the graphite intercalation compounds (GIC) and the doped polymers. Although GIC have been known since the last century, research in the field has received renewed impetus with the discovery that upon intercalating graphite with AsF_5 and SbF_5, the electrical conductivity can increase by a factor of 10-15, approaching that of copper [1,2].

More recently, doped polymers have attracted attention, because it was found that by doping certain polymers such as polyacetylene with donors or acceptors, increases in electrical conductivity by many orders of magnitude may be observed [3].

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Regarding the GIC one of the pertinent questions has been: "Can we relate the increased conductivity to the chemical reaction taking place upon intercalation and to the nature of the intercalated species"? The ability to answer such questions might conceivably enable us to design lightweight electrical conductors with desirable properties. This problem has been the subject of lively controversy and even today is not fully resolved. Most of the controversy has revolved about the nature of the species in GIC intercalated with AsF_5.

The reaction occurring in the presence of excess AsF_5 is [4]

$$8C + AsF_5 \rightarrow C_8AsF_5 \text{ (stage I)} \quad (1)$$

However, this equation only gives the overall stoichiometry, but no detailed insight into the chemistry.

Bartlett [5] proposed that the following reaction goes to completion upon intercalation,

$$3AsF_5 + 2e \rightarrow 2AsF_6^- + AsF_3 \quad (2)$$

while others [6,7] claimed that the material also contains neutral AsF_5; i.e., for stage I the reaction may be written as

$$8C + AsF_5 \rightarrow C_8^{+2y/3}(AsF_6^-)_{2y/3}(AsF_3)_{y/3}(AsF_5)_{1-y} \quad (3)$$

where according to Bartlett, $y = 1$, while others [7] estimate y as low as $\simeq 0.4$. The quantity $2y/3$ here would be the degree of charge transfer per intercalated AsF_5. The determination of this quantity is problematical, the results often varying with the type of physical measurement applied.

In the following we restrict ourselves to the family of GIC with the 4d and 5d transition metal hexafluorides (MF_6) where the intercalated species can serve as a magnetic probe to ascertain its identity.

Intercalation compounds of graphite with OsF_6, IrF_6 and PtF_6 have been reported by Bartlett, et al. [8]. On the basis of magnetic susceptibility measurements on the powdered materials, the intercalate species have been identified as OsF_6^-, IrF_6^- and PtF_6^{-2}, respectively [8].

While the hexafluorides have many physical properties which vary monotonically in a given series as a function of the atomic number of the metal, they are all isostructural and nearly isodimensional. In the 5d series, for example, the M-F bond lengths range from 1.833 Å (WF_6) to 1.830 Å (IrF_6) while for MoF_6, Mo-F is 1.820 Å. Furthermore, the average bond distance in OsF_6^- is nearly the same (1.82 Å). For a given stoichiometry of the GIC, such as C_8MF_6, the lattice energy of the latter should thus be independent of M. Therefore, the only variable in a thermodynamic cycle comparing

different MF_6 would be the electron affinity (EA) of MF_6. This should be large enough to overcome the energy required to separate the graphite layers as well as the unfavorable entropy term arising from ordering of the guest species between the layers [8,9].

Bartlett has estimated that the free energy ($-\Delta G°_{298}$) of the reaction

$$MF_6(g) + e \rightarrow MF_6^-(g) \qquad (4)$$

must exceed 120 kcal/mole for spontaneous intercalation to occur [9]. Only WF_6, for which the EA is 104 kcal/mole, does not meet this criterion, and indeed it does not intercalate into graphite by itself. All other hexafluorides of the 4d and 5d series which have been tried do intercalate. The EA of the MF_6 have been obtained for the group VI hexafluorides (M = Mo, W, U) from electron attachment coefficients in a mass spectrometer. That for PtF_6 has been calculated from a thermochemical cycle for the formation of $O_2^+PtF_6^-$. All others have been estimated based on their relative reactions with nitric oxide and nitrosyl fluoride [8,9].

We have investigated the intercalation of graphite with a number of transition metal MF_6 and determined some of the magnetic and electrical properties of the resulting GIC. In these reactions the increasing oxidizing properties of the MF_6 along a given series can be related to some of the electrical and magnetic properties, which in turn gives us a firmer basis for the estimation of the EA.

The graphite material used was in all cases highly oriented pyrolytic graphite (HOPG), which has essentially single crystal properties along the c-axis but some mosaic spread in the a-plane. As expected, it and its GIC exhibit strongly anisotropic properties. The best understood system to date is HOPG/OsF_6 [10].

This material gives a strong ESR signal which is highly anisotropic and not observable in powdered material. The variation of the g-factor as a function of the orientation of the c-axis of the HOPG slab with respect to the magnetic field is given by Fig. 1. It obeys the relation

$$g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta \qquad (5)$$

where $g_{\parallel} = 1.65 \pm 0.05$ and $g_{\perp} = 3.25 \pm 0.05$; i.e., $g_{\perp} \approx 2g_{\parallel}$. The intensity of the signal shows Curie-like behavior and no evidence for a magnetic transition is seen down to T = 2K. The ESR linewidths increase appreciably for samples kept in quartz tubing for several months. However, the spin density as obtained from magnetic susceptibility measurements does not change. Parallel changes are observed in the X-ray diffraction spectra, as has already been reported by Bartlett [8].

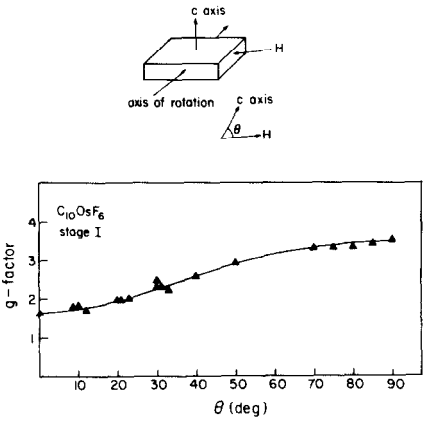

Fig. 1. The anisotropy of the g-factor for stage I, HOPG/OsF_6, i.e. g-factor vs. orientation of the HOPG in the magnetic field.

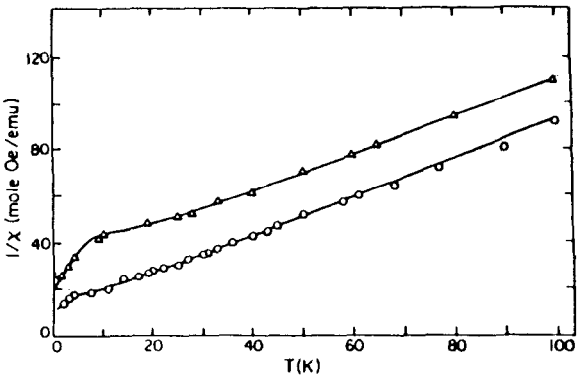

Fig. 2. Inverse longitudinal susceptibility, $1/\chi_{\parallel}$(triangles) and the inverse transverse susceptibility $1/\chi_{\perp}$(circles) of stage I HOPG/OsF_6 vs. temperature.

The inverse susceptibilities of stage I (HOPG/OsF_6) are given in Fig. 2. It shows that $1/\chi_{\parallel}$ increases steeply at low temperature with a 'knee' a around 15 K, then increases more moderately at high temperatures. In

contrast, $1/\chi_{\perp}$ increases linearly over the whole temperature range. At higher temperatures both curves have the same slope; namely, one corresponding to a magnetic moment of 3.2 μ_B as observed by Bartlett for powdered materials. The magnetic moments can be explained in terms of a degenerate quartet ground state of the $5d^3$ configuration of the OsF_6^- species. The ^4F term corresponding to the free ion with d^3 configuration is split into three states ($^4A_2$, $^4T_2$, $^4T_1$) in an octahedral symmetry as shown in Fig. 3. A slight distorsion of the octahedral symmetry affects

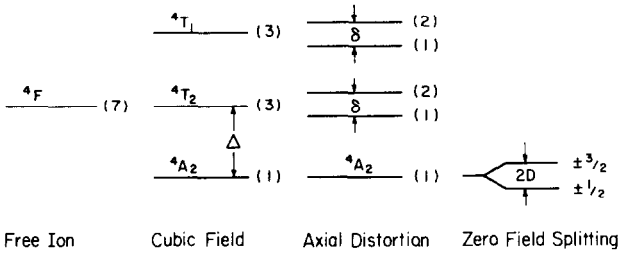

Fig. 3. The splitting of energy levels for a d^3 configuration in an octahedral environment and by slight axial distortion.

the orbital degeneracy of the T_2, T_1 states leading to a splitting of each triplet to a singlet and a doublet, separated by an energy δ. Furthermore, the spin-orbit coupling partially removes the degeneracy of the ground state, ^4A, leading to a zero magnetic field splitting of the quartet into two doublets (± 3/2, ± 1/2) with energy splitting 2D. The energy levels corresponding to these states have been calculated and correctly predict the experimentally observed $g_{\perp} \approx 2g_{\parallel}$ [10].

The observation of Curie-Weiss behavior at higher temperatures show the importance of spin-spin interaction. The spin-Hamiltonian of the quartet has accordingly been modified. Solving this modified Hamiltonian leads to expressions of the Weiss constants in terms of the spin-spin exchange parameters, $J_{\parallel}$ and $J_{\perp}$, and the singlet-triplet splitting, Δ. Using the value g = 1.65 from ESR one obtains a good fit (solid line) to the experimental susceptibilities with the parameters, $J_{\parallel} = -11\ cm^{-1}$, $J_{\perp} = -8\ cm^{-1}$ and $D = 9\ cm^{-1}$. Knowledge of D and g enable one to estimate

λ/Δ and the distortion energy δ from the well known relations, where λ is the spin-orbit coupling

$$g = 2(1 - 8\lambda/D); \qquad 2D = 8\lambda^2\delta/\Delta^2 \tag{6}$$

At high temperatures the isotropic magnetic moment is given by $\mu_{eff} = g\sqrt{S(S+1)}\ \mu_B$. Using S = 3/2 and g = 1.65 one obtains $\mu_{eff} = 3.2\ \mu_B$, in excellent agreement with the experimental value.

The above shows that the intercalation of OsF_6 involves complete charge transfer of one electron per OsF_6 giving an intercalated species OsF_6^-; i.e. a degree of charge transfer, x = 1. Moreover, the results provide evidence of a well-defined crystal field and a well-defined orientation of the OsF_6^- within the graphite layers. This is consistent with Bartlett's suggestion that the C_3 axis of the OsF_6^- ion is parallel to the graphite c-axis [8]. The value of x = 1 is significantly larger than that observed previously for the AsF_5 system.

Another system to be investigated was that of HOPG/MoF_6 [11]. Molybdenum hexafluoride has a much lower electron affinity (131 Kcal/mole) than that estimated for OsF_6 (154 Kcal/mole). The degree of charge transfer might thus be expected to be less than for OsF_6. In contrast to the latter, intercalation proceeds best by contacting the HOPG with liquid MoF_6 (m.p., 17.4°C), and even then intercalation proceeds extremely slowly, reaching stage I only after about five days. Also, in contrast to OsF_6, the specific conductivity per graphite layer increases stepwise. However, the plateaus do not correspond to well-defined stages except at the very end of the intercalation when stage I is attained. Intermediate plateaus correspond to mixtures of stages. These jumps may correspond to noncontinuous charge transfer associated with weight uptake and filling of layers. HOPG/MoF_6 also differs from the OsF_6 system in that the final conductivity attained is about 5.5 times that of pristine HOPG, while with OsF_6 catastrophic conductivity decrease is seen as stage I is approached.

The HOPG/MOF_6 system also differs significantly from OsF_6 in its magnetic properties. In contrast to the latter where in the ESR only one signal arising from a localized species is observed, the MoF_6 system displays two signals for stages I and II and an additional weak signal for stage III (Fig. 4) labelled d, c_1 and c_2, respectively.

The two main signals are believed to arise from two different species, because they show different temperature dependences. Signal d appears at g = 1.60 ± 0.05. It shows slight anisotropy, but its intensity varies roughly as 1/T as expected for a paramagnetic species. It is assigned to

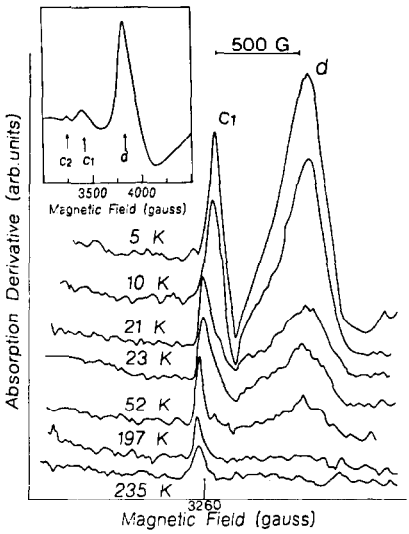

Fig. 4. ESR spectra of stage I HOPG/MoF_6 for H||C (see Fig. 1) at various temperatures. Inset shows ESR spectrum of stage III at T = 6 K. An additional signal C_2 is seen.

an intercalated $5d^1$ species corresponding to the $MoF_6^-(V)$ ion. Its relatively broad line width is attributed to unresolved hyperfine interaction with the ^{95}Mo and ^{97}Mo nuclei.

Signal c_1, at approximately $g \approx 1.89$, is angularly independent. However, it shows a slight temperature dependence in g-value changing from g = 1.89 at 4 K to g = 1.99 at 300 K. This signal is believed to be associated with conduction carriers. Normally this would not show intensity variations with temperature. Indeed it is still visible at room temperature in contrast to signal d. However, the temperature dependence of c_1 can be explained by exchange with the localized species (d). Since the value of g_d is almost unaffected by this exchange, we can estimate the effective magnetic moment of the Mo^{+5} ions assuming S = 1/2 and g_d = 1.6; e.g.,

$$\mu_{ESR} = g_d \sqrt{S(S+1)}\mu_B = 1.4\ \mu_B \qquad (7)$$

In reality the susceptibility behaves according to

$$\chi = \frac{N\mu_{eff}^2}{3K(T+\theta)} + \chi_0 \qquad (8)$$

that is, it has a relatively large T.I.P. From the temperature dependent component one obtains a magnetic moment, $\mu_{eff} = 0.63\ \mu_B$ and $\theta = 3$ K. The discrepancy between the observed moment and that calculated from ESR can be resolved by assuming that not all the intercalated MoF_6 is reduced to MoF_6^-. Accordingly, the degree of charge transfer x is

$$x = \left(\frac{\mu_{eff}}{\mu_{ESR}}\right)^2 = \left(\frac{0.63}{1.4}\right)^2 = 0.2$$

i.e. only 20% of the intercalated MoF_6 is reduced, and the intercalation reaction may be written

$$nC + MoF_6 \rightarrow C_n^{+0.2}(MoF_6^-)_{0.2}(MoF_6)_{0.8} \qquad (9)$$

Another interesting feature of the MoF_6 system is the observation of a weak additional signal for stage III at $g \approx 2$. This signal is attributable to a graphite interior layer not adjacent to an intercalate layer. This signal, c_2, is angularly independent in contrast to the graphite signal in pure HOPG which shows an anisotropy of 70 Gauss in the field of resonance [12]. This isotropic signal c_2 in stage III HOPG/MoF_6 indicates therefore significant charge transfer to graphite interior layers. This is consistent with work by Safran [13] and others who have demonstrated long range charge screening by charged intercalate layers.

We see therefore a remarkable difference between the highly electronegative OsF_6 and the less electronegative MoF_6. The question is whether this difference extends to other MF_6. If yes, one would expect ReF_6 (estimated E.A. 129 Kcal/mole) to behave like MoF_6 (E.A. = 131Kcal/mole).

Contrary to earlier reports, ReF_6 does intercalate into graphite, albeit extremely slowly [14]. The intercalation works best by contacting the HOPG with liquid ReF_6 (m.p. 18.5°C), and even then stage I is reached only after about three weeks. In contrast to OsF_6, the conductivity increases smoothly reaching an asymptotic value of $\sigma/\sigma_g \approx 6.5$ for stage I. No plateaus similar to those with MoF_6 were observed. Neither is an ESR signal observed down to 2 K, but no resonance associated with a d^2 configuration has ever been observed in a metallic environment.

Magnetic susceptibility measurements show that stage I HOPG/ReF_6 has an effective magnetic moment of 1.25 μ_B, which falls between that of neutral ReF_6 ($\mu_{eff} = 0.25\ \mu_B$) and that of ReF_6^- in the alkali hexafluoro rhenates ($\mu_{eff} = 1.5 - 2.1\ \mu_B$). We estimate the degree of charge transfer by assuming that the moment of the intercalate species is the average of ReF_6 and ReF_6^- moments (for the moment of ReF_6^- we take that of $KReF_6$,

$\mu_{eff} = 2.1\ \mu_B$). Solving

$$(1.25)^2 = (1-x)(0.25)^2 + (2.1)^2\ x$$

we obtain $x = 0.35$; i.e.

$$nC + ReF_6 \rightarrow C_n^{+0.35}(ReF_6^-)_{0.35}(ReF_6)_{0.65} \qquad (10)$$

It should be emphasized that all above estimates for degree of charge transfer relate to the stage I compounds. The charge transfer may, however, be a function of stage. This is particularly exemplified by the ReF_6 system.

If (00ℓ) diffraction patterns of HOPG/ReF_6 are obtained shortly after pumping off the excess ReF_6 after the three weeks exposure (Fig. 5), one obtains a clear pattern of stage I with d = 8.35 Å. In addition, a small amount of a second phase, a stage I' compound with d = 8.12 Å, is seen. Upon running (00ℓ) diffractograms successively, one sees a gradual disappearance of stage I and the appearance of stage II and later stage III. After about 16 hours only pure stage IV is seen, which appears to be stable. The filled layer spacings of stages II-IV do not conform to those calculated from stage I with the formula $d = 8.35 + 3.35\ (n - 1)$ Å. They are smaller. It appears that neutral ReF_6 is released as a function of time. Thus, as we go to higher stages the ReF_6^-/ReF_6 ratio increases as well as the degree of charge transfer per intercalated ReF_6. The origin of stage I with d = 8.12 Å is unknown. It may be due to the presence of domains of pure $C_n^+ReF_6^-$ with $x = 1$, similar to $C_n^+OsF_6^-$.

Graphite compounds with TcF_6 would be expected to be more similar to those of OsF_6, based on the known oxidizing power of TcF_6 [15]. Upon exposure of HOPG to TcF_6, the conductivity rises rapidly reaching a maximum $\sigma/\sigma_g \simeq 7$ at about stage II which has a d-spacing of 11.46 Å. Upon further exposure, stage I is reached with a d-spacing of 8.12 Å, the same as for stage I $C_n^+OsF_6^-$. Similarly, the conductivity falls to that or below that of HOPG.

The ESR spectrum of $C_{10}TcF_6$ (stage I) at 4K gives a clearly resolved 10-line spectrum as expected for a ^{99}Tc species with spin I = 9/2 (Fig. 6). The properties of this spectrum, $g \simeq 2$, hyperfine splitting A = 330 G, fit a d^1 species, as they are similar to other hexavalent technetium complexes. It is possible that this spectrum arises from a small amount of intercalated neutral TcF_6, while the major fraction of TcF_6^- does not give a signal. However, this is in conflict with magnetic susceptibility data. Stage I

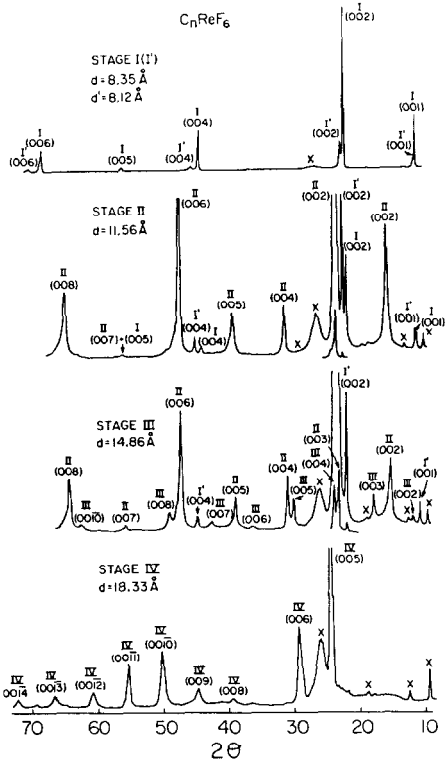

Fig. 5. (001) diffractograms of HOPG/ReF_6 as a function of time.

(a) ½ hr.
(b) 1½ hr.
(c) 3 hr.
(d) 16 hr.

after removing excess ReF_6. Note contraction of the filled layer spacing with increasing stage.

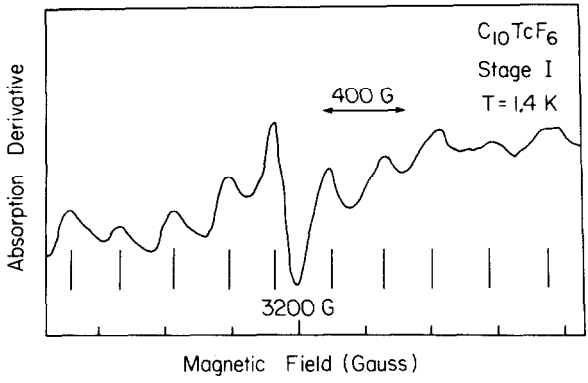

Fig. 6. ESR spectrum of stage I $C_{10}TcF_6$. Note 10-line spectrum as expected from Tc species with spin I = 9/2.

$C_{10}TcF_6$ has an effective moment, $\mu_{eff} = 0.7\ \mu_B$ ($\theta = 3K$). This falls between that of neutral TcF_6 ($\mu_{eff} = 0.45\ \mu_B$) and that of TcF_6^- in the alkali hexafluorotechnetates (V), ($\mu_{eff} = 2.25 - 2.51\ \mu_B$). Calculations similar to those performed above for the ReF_6 system lead to the unlikely degree of charge transfer of $x = 0.06$. For the moment we assume that $x = 1$, in keeping with the known oxidizing power of TcF_6 and the d-spacing of the stage I compound, which is the same as for OsF_6.

As we have seen the hexafluorides span the gamut from very electronegative ones to relatively mild oxidizers. At one end we have PtF_6 for which $x = 2$. At the other end we find MoF_6 and ReF_6 for which $x < 1$. The electrical conductivities vary with x. For $x \geq 1$, we observe catastrophic conductivity decrease as we reach stage I. For $x < 1$ the final conductivities even for stage I, are between 5-8 times that of HOPG.

It is interesting to note two important features of the conductivity of the acceptor type compounds. First, as mentioned above, all the acceptor compounds exhibit a maximum in conductivity (minimum in the resistivity, ρ_{min}) versus the intercalant concentration at 300K. The values of ρ_{min} (Table I) occur for certain values of n in C_nMF_6 which are given in Table I. Knowledge of n and x (charge transfer per intercalated MF_6) enables one to estimate the charge transfer per carbon (as x/n). This value is also given in Table I. As clearly seen, the maximum in conductivity occurs for a charge transfer per carbon of approximately $x/n \sim 0.04$, a fact that was pointed out by others [7]. Furthermore, the reduction of the electrical conductivity beyond this limit, is either due to the formation of covalent bonds which act as carrier scattering centers or due to lattice instabilities induced by overcharging the graphitic layers. Conductivity measurements combined with weight uptake can give a rough estimate of charge transfer. The second feature is that even when charging of the layers is not complete; i.e., lower than the limit mentioned above, in all cases, there is a decrease of the conductivity in stage I, a fact that supports the idea that there is a strong contribution to the scattering of the π electrons by the intercalate species, which in this case is bounding the graphite layers from both sides. Table I shows the room temperature resistivities of stage I compounds, ρ(stage I), which is indeed larger than ρ_{min}.

Further analogies are seen in the temperature dependences of the resistivities. The in-plane resistivity of intercalation compounds can be expressed in terms of temperature dependent and temperature independent components.

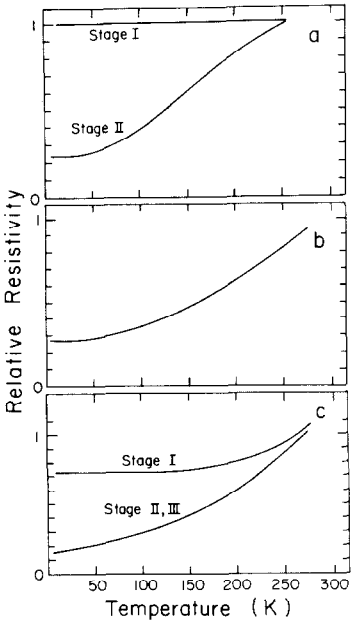

Fig. 7.

7a. The relative electrical resistivities of HOPG/OsF_6 (stages I and II) vs. temperature.

7b. The relative electrical resistivities of HOPG/ReF_6 (stages I and II) vs. temperature.

7c. The relative electrical resistivities of HOPG/TcF_6 (stages I or II) vs. temperature.

$$\rho_a(t) = A + BT + CT^2 \qquad (11)$$

A originates from defects or impurity scattering, whereas B and C are due to electron-phonon and electron-electron scattering [16]. In Fig. 7a we see that the resistivity of stage I C/OsF_6 is temperature independent; i.e., dominated by defect scattering, while stage II displays normal metallic behavior. The less electronegative MF_6 such as MoF_6 and ReF_6 with low degree of charge transfer show metallic behavior even for stage I (Fig. 7b). For TcF_6 the temperature dependence is normal for stages II and III, while the stage I compound is similar to stage I C/OsF_6 (Fig. 7c). Stage I C/TcF_6 shows, however, some temperature dependence which may indicate the possibility of a phase transition as the cause of change in slope. These data are summarized in Table II.

In the foregoing we have estimated the degree of charge transfer, x, upon intercalation of various MF_6 using the magnetic properties of the

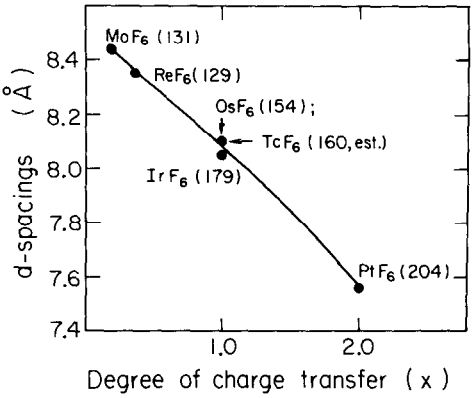

Fig. 8. The filled layer spacing (d) vs. degree of charge transfer (x) for different MF_6. The estimated E.A. of the MF_6 are given in parentheses. That for TcF_6 could actually be somewhat less than OsF_6.

intercalate species. Some of these estimates were based on possibly questionable assumptions. We may, however, gain confidence in these estimates by correlating x with the d-spacings of the stage I compounds. In Fig. 8, we see a smooth correlation between these parameters. For ReF_6 and MoF_6 we have taken the largest d-spacings observed. For those compounds this parameter may vary somewhat depending on the amount of neutral MF_6 intercalated. For MoF_6, for example, d varies between 8.35 and 8.45 Å. It can be seen from Fig. 8 that the assumption of x = 1 for TcF_6 is reasonable despite the conflict with the magnetic results. The value of x = 2 for PtF_6 is based on the identification of the intercalate as PtF_6^{2-} as inferred from magnetic susceptibility measurements (8). It appears from this that in the IrF_6 system, x may be greater than 1, since the d-spacing of 8.05 Å is somewhat less than that for OsF_6. This could mean that IrF_6 is partially reduced to IrF_6^{2-} upon intercalation; i.e. $x > 1$. The aberrant behavior of IrF_6 is seen more clearly in a plot of x vs. E.A. (Fig. 9). Only IrF_6 deviates substantially from a relatively smooth correlation implying that IrF_6 is partially reduced to IrF_6^{2-} ($x > 1$) and/or that the E.A. of IrF_6 is lower than that previously estimated. The electron affinity of IrF_6 has been derived from the optical spectra of Xe/IrF_6 gas mixtures [17]. The calculated value of 181 Kcal/mole is close to that estimated by Bartlett (179 Kcal/mole), indicating that x is indeed greater than 1. Another possible conclusion from Fig. 9 may be that ReF_6 has a higher E.A. than MoF_6.

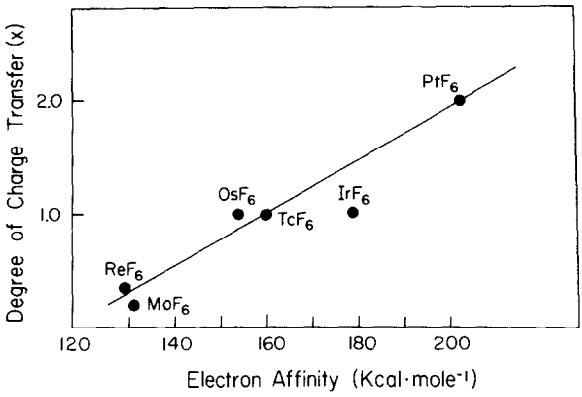

Fig. 9. Estimated degree of charge transfer (x) vs. the estimated E.A. of MF_6. Note aberrant behavior of IrF_6. The straight line is given as guide to the eye.

It is of interest to compare the results of intercalation of MF_6 into graphite with doping of polyacetylene by MF_6. Many hexafluorides including WF_6 dope $(CH)_x$ to the metallic state [18]. It has been shown that there exists an inverse relation between the maximum conductivity attainable with a given MF_6 and its electron affinity. The only exception to this correlation is again IrF_6, which gives a maximum conductivity actually larger than that expected from this inverse correlation.

It is quite reasonable to assume that the chemical reaction upon doping of polyacetylene is similar to that upon intercalation of graphite. However, thus far it has not been possible to identify any of the doped species by magnetic methods. ESR measurements of $(CH)_x$ doped with WF_6, MoF_6, ReF_6, and UF_6 yield spectral characteristic of the polymer chain but not of the presumably reduced MF_6 species [19]. The possibility of formation of spin-paired $(MF_6^-)_n$ species cannot be ruled out. However, it is not clear why spin-pairing should obtain in doped polymers and not in intercalated graphite.

The foregoing has shown that a certain group of inorganic fluorides, the MF_6, has played an important role in answering (partially) some of the outstanding questions in intercalation chemistry. Fluorine chemistry, however, plays a much greater role in this field than the above suggests. A full discussion of this would be beyond the scope of this discussion. Other important aspects of the field have been discussed elsewhere [20].

TABLE 1

Material	ρ_{min} ($\mu\Omega$-cm) T=300K	n(at min ρ)	Charge Transfer per Carbon (x/n)	ρ(stage I) ($\mu\Omega$-cm) T=300K
C_nAsF_5	1.6	16	0.025	2.1
C_nOsF_6	2	25-27	0.04	80-100
C_nMoF_6	3-4	$\approx$ 16	$\approx$ 0.01	6-7
C_nReF_6	3-4	$\approx$ 16	$\approx$ 0.01	6-7
C_nTcF_6	3	$\approx$ 20	$\approx$ 0.05	40-50
C_nIrF_6	2.5	25	0.04	80-100

TABLE II

Material	Stage	A($\mu\Omega$-cm)	B($\mu\Omega$-cm-K^{-1})	C($\mu\Omega$-cm-K^{-2})
$C_{17}ReF_6$	I	1.6	6.8×10^{-3}	3.3×10^{-5}
$C_{10}MoF_6$	I	1.95	2×10^{-3}	6.5×10^{-5}
C_9TcF_6	I	$\approx$ 30	almost constant	
$C_{20}TcF_6$	II	0.9	1.6×10^{-3}	5.7×10^{-5}
$C_{10}OsF_6$	I	80	almost constant	
$C_{27}OsF_6$	III	0.64	2.7×10^{-3}	6×10^{-6}
$C_{30}OsF_6$		0.94	4.1×10^{-3}	4×20^{-5}

$$\rho(T) = A + BT + CT^2$$

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