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Charge transfer in stage-1 OsF_6- and MoF_6-intercalated graphite compounds

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The charge transfer per carbon atom has been studied in stage-1 C_nOsF_6 and C_nMoF_6. Optical reflection measurements in the range 0.8–3 eV yield a charge transfer per carbon atom of $f_{C(\mathrm{elec})}=0.035$ and 0.029, respectively. The shifts in the energy of the Raman lines with the symmetry $\hat{E}_{2g_2}$ are correlated with a difference of 0.01 in the electronic charge transfer per carbon for these compounds. These results are compared with recent ESR susceptibility measurements on these compounds which yield the chemical charge transfer per intercalated MF_6 (M =Os,Mo) molecule. These were $f_{M(\mathrm{chem})}=1$ and 0.2, respectively. The large discrepancy for C_nOsF_6 ($f_{M(\mathrm{chem})}:f_{M(\mathrm{elec})}=3:1$) indicates a rather strong interaction between the carbon atoms and the fluorine atoms of the intercalate.

INTRODUCTION

An important aspect of the investigations of graphite intercalation compounds (GIC's) has been the interaction between the intercalant species and the host material.[1] Weak oxidizing species display an electrostatic interaction with the carbon layers and the positive charges transferred to the carbon layers are delocalized. Strong oxidizing species produce bonds with a partially covalent character, and therefore the positive transferred charges are localized. Several workers[2–5] have suggested that in lightly doped compounds the guest-host interaction is mainly ionic. However, above a certain free-charge density (0.03–0.05 holes per carbon atom) covalent bonds are formed. This suggestion relied upon several experimental results. Ubbelohde and co-workers[3,4] observed that during electrolytic intercalation of H_2SO_4 a limiting charge transfer is reached. The maximum in the in-plane conductivity of the stage-2 or -3 phases has been attributed by Fischer[5] to the creation of covalent bonds which act as scattering centers. X-ray photoemission spectra[6] indicate that in high-concentration $C_nH_2SO_4$ compounds covalent bonds are formed between the carbon and the oxygen atoms; namely, carbon atoms in the graphite layers have an sp^3 configuration. Furthermore, reflectivity measurements indicate that the energy of the plasma edge increases upon increasing the intercalant concentration. However, above a certain intercalant concentration the plasma edge is saturated. Increasing the charge transfer by either fluorinating the analogous C_nAsF_5 compounds[7] or by overoxidizing the $C_nH_2SO_4$ system[6,8] resulted only in a decrease of the plasma-edge slope. The minimum of the reflectivity did not change.

In this work we examine this problem by measuring the charge transfer per carbon atom in two stage-1 compounds: C_nOsF_6 and C_nMoF_6. These compounds are special, because the charge transfer can be measured by either probing the intercalated metals or the graphite layers. The former is done through ESR and magnetic susceptibility measurements.[9,10] A comparison between the different experiments gives information concerning the fraction of bonds with covalent characteristics in these compounds.

EXPERIMENTAL DETAILS AND RESULTS

Stage-1 C_nOsF_6 and C_nMoF_6 compounds were prepared as described elsewhere.[9,10] After the intercalation process they were characterized by weight uptake and by (001) x-ray diffraction. The stoichiometric formula for the pure stage-1 phase is $C_{8-11}MF_6$ (where M=Os,Mo) and the c-axis repeat distances were $I_c=8.0$–8.1 Å for C_nOsF_6 and $I_c=8.35$–8.45 Å for C_nMoF_6. The samples for optical measurements were sealed into a sample holder in a dry box. Near-normal reflectivity measurements were performed with a grating monochromator (Perkin-Elmer E1) using a tungsten-filament source. A reflector (Al mirror), which was substituted at each wavelength, was used as a reference. The Raman measurements were taken on a home-built digitally controlled triple monochromator.[11]

The reflectivity measurements presented in Fig. 1 were taken on $C_{10.8}OsF_6$ and $C_{8.7}MoF_6$. The dots are the experimental points and the solid lines are fits to the Blinowski-Rigaux model described later on. The minimum in the reflectivity of C_nOsF_6 is located at 1.78 eV, 0.2 eV higher than the minimum in the reflectivity of C_nMoF_6. The slope of the plasma edge of C_nMoF_6 is much steeper than that of C_nOsF_6.

The Raman measurements are presented in Fig. 2. The

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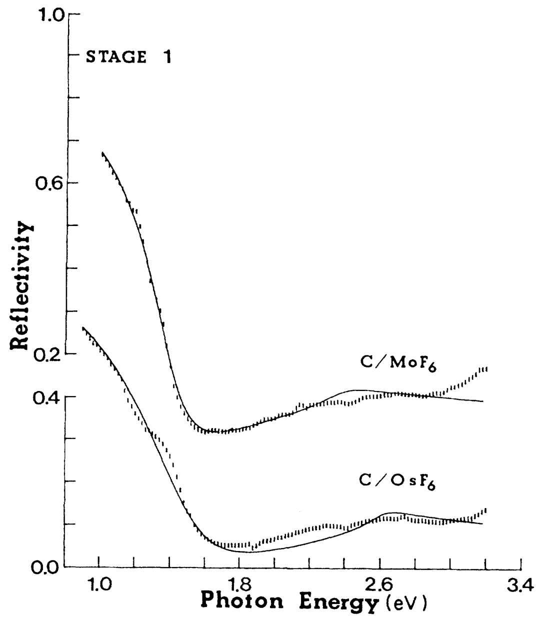

FIG. 1. Reflectivity spectra of state 1: (a) C_nOsF_6 and (b) C_nMoF_6. The dots are the experimental results and the solid lines are fits to the Blinowski-Rigaux model (Ref. 12).

frequencies of the Raman line with the $\hat{E}_{2g_2}$ symmetry for the two compounds are $\omega = 1639$ cm^{-1} and 1634 cm^{-1} for C_nOsF_6 and C_nMoF_6, respectively. The linewidths at half maximum are $\Gamma = 12$ and 9 cm^{-1}, respectively. The spectra of the C_nOsF_6 compound exhibit an additional broad line at 1360 cm^{-1}.

ANALYSIS

Reflectivity measurements are sensitive to the number of free-charge carriers on the graphite layer. The data were analyzed in terms of the Blinowski-Rigaux[12] two-dimensional (2D) tight-binding model. In this model the c-axis interaction is reduced and the π electronic bands are linear functions of k, the 2D wave vector. The complex dielectric function is composed of an intraband term, described by the Drude relation, and an interband term resulting from a valence-to-conduction-band electronic transition. The fitting procedure yields the plasma frequency ω_p and the lifetime of the free-charge carriers. The first is related to the shift in the Fermi energy level and to the electronic free-charge transfer per carbon atom, $f_{C(\text{elec})}$ through

$$\omega_p^2 = \frac{4e^2}{\hbar^2 I_c} E_F \tag{1}$$

and

$$f_{C(\text{elec})} = \frac{1}{\sqrt{3}\pi}\left[\frac{E_F}{\gamma_0}\right]^2 , \tag{2}$$

where γ_0 is the overlap integral between π electrons of nearest-neighbor carbon atoms in the same plane. (The notation used here for the different kinds of charge transfer is compatible with that in Ref. 7.) The best fits give the following values: $C_{10.8}OsF_6$: $f_{C(\text{elec})} = 0.035 \pm 0.003$ and $\tau = 1.8$ eV^{-1}; $C_{8.7}MoF_6$: $f_{C(\text{elec})} = 0.029 \pm 0.03$ and $\tau = 4$ eV^{-1}. γ_0 is taken to be 3 eV (Ref. 13) with a possible deviation of ±10%.

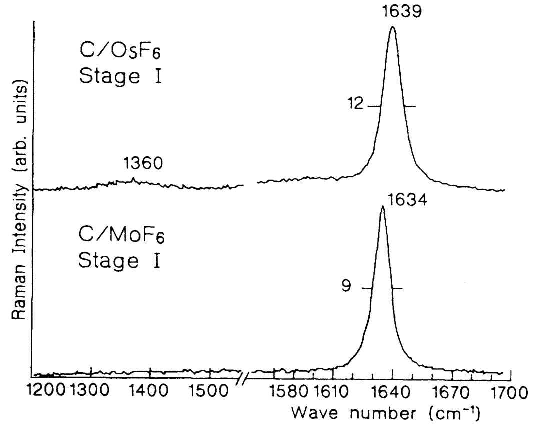

FIG. 2. Raman spectra of stage 1: (a) C_nOsF_6 and (b) C_nMoF_6. The high-frequency lines in the two spectra are assigned to the C-C vibration with $\hat{E}_{2g_2}$ symmetry. The line at 1360 cm^{-1} is identified with off-zone-center phonons.

The Raman line with the $\hat{E}_{2g_2}$ symmetry in acceptor GIC's is shifted up upon decreasing the stage index. Pietronero and Strassler[14] have shown that the shift is due to contraction of the in-plane C—C bond distance resulting mainly from the net free-charge carriers on the graphite layers. Kamitakahara *et al.*[15] have recently measured this contraction in the C—C bond distance in $C_nD_2SO_4$ and Eklund *et al.*[16] have correlated it, experimentally, with the shift of the frequency of the $\hat{E}_{2g_2}$ mode. For the stage-1 phase they have obtained an experimental linear dependence between the frequency and the charge transfer:

$$\omega(\hat{E}_{2g_2}) = \omega_0 + A f_{C(\text{elec})} , \tag{3}$$

where $A = 460 \pm 30$ cm^{-1}. ω_0 has a weak dependence on the intercalant characteristics; namely, on the c-axis repeat distance and on the carbon-intercalant interaction. Therefore, we can assume that for our compounds ω_0 is approximately equal, thus yielding

$$f_{C(\text{elec})}(C_nOsF_6) - f_{C(\text{elec})}(C_nMoF_6) \sim 0.01 . \tag{4}$$

Note, that the linear relationship reported in Ref. 15 breaks down under "overoxidizing" conditions and the Raman shift is saturated. Therefore, Eq. (4) should be treated with caution. However, in any case $f_{C(\text{elec})}(C_nOsF_6) \gtrsim f_{C(\text{elec})}(C_nMoF_6)$.

DISCUSSION

The transition-metal hexafluorides OsF_6 and MoF_6 possess characteristic magnetic properties in their intercalated form. Hence ESR and magnetic susceptibility measurements on those systems yield information concerning

TABLE I. The values of the chemical and electronic charge transfer (per carbon and per molecule) measured by different techniques. The numbers not in parentheses are the measured values, whereas the numbers in parentheses were derived from the former by taking $n=9$ as a characteristic value for stage-1 C_nMF_6 (M=Os;Mo).

		C_nMoF_6	C_nOsF_6
ESR +	$f_{M(\text{chem})}$	$0.2\pm15\%$	$1\pm15\%$
Magnetic susceptibility	$f_{C(\text{chem})}$	(0.022)	(0.11)
Reflectivity	$f_{M(\text{elec})}$	(0.261)	(0.315)
	$f_{C(\text{elec})}$	$0.029\pm10\%$	$0.035\pm10\%$
Raman measurements		$f_{C(\text{elec})}(C_nOsF_6)-f_{C(\text{elec})}(C_nMoF_6)\cong 0.01$	

the electronic configuration near the metals. It has been found[9,10] that the intercalate species in the first compound is OsF_6^-; e.g., there is a charge transfer of one electron (or almost one) per molecule. The results for the second case show that a large fraction of the intercalant molecules remains neutral. More precisely, the charge transfer per MoF_6 molecule, $f_{M(\text{chem})}$, is approximately 0.2. In Table I we summarize the information on the charge transfer $f_{C(\text{elec})}$ and $f_{M(\text{chem})}$ from the different experimental techniques. The results for stage-1 C_nMoF_6 from the different measurements are consistent. However, this is not the case for C_nOsF_6, where the results differ by a factor of 3. The discrepancy is due to the fact that reflectivity measurements probe the graphite layers and, here, the number of free-charge carriers. ESR-susceptibility techniques probe the intercalant species and therefore measure the number of electrons transferred from the carbon layers. We can thus conclude that in C_nMoF_6 all the positive charges transferred are free on the carbon layers. However, stage-1 C_nOsF_6 is a very special system in which only 38% of the holes on the graphite layers are free, while the rest interact rather strongly with the fluorine atoms and form bonds with partial covalent character.[6–8] Some of the free charges are therefore localized. The in-plane conductivities of these compounds[17] are in good agreement with the above description. In C_nMoF_6 the conductivity reaches a maximum of $\sigma/\sigma_{\text{HOPG}}=10$–$13$ for $C_{16}MoF_6$ (stage-2) and then decreases slightly to a ratio of $\sigma/\sigma_{\text{HOPG}}=5$–$6$ for C_8MoF_6 [σ_{HOPG} is the conductivity of highly oriented pyrolytic graphite (HOPG).] The maximum conductivity ($\sigma/\sigma_{\text{HOPG}}=18$–$20$) of C_nOsF_6 compounds occurs at $C_{27}OsF_6$ (stage 3) which corresponds to an electronic charge transfer of 0.037 holes per carbon. For the stage-1 compound the conductivity ratio decreases to a value which is even smaller than that of the graphite (~ 0.5). In this concentration region some of the intercalate species form stronger bonds with the carbon atoms and localize the holes. These localized charges act as scattering centers and reduce the carrier mean free path. This is supported by recent electrical conductivity studies[17] on these materials, which show that the stage-1 C_nOsF_6 conductivity is temperature independent down to 4 K. Furthermore, the high residual resistivity of this compound has been analyzed in terms of a simple Drude model which yields a mean free path of the order of 10–50 Å.

The Raman measurements support the above discussion. The relative shift in the frequencies of the lines with the $\hat{E}_{2g_2}$ symmetry corresponds to the difference in the free-charge transfer per carbon atom in the two compounds. The estimated difference in the values of the free-charge transfer per carbon is ~ 0.01 and is in good agreement with the reflectivity measurements. An important feature in the Raman results is the observation of a broad line at 1360 cm^{-1} in the C-OsF_6 spectra. It is identified as disorder-induced Raman scattering of off-zone-center phonons.[18,19] The disorder is due to the strong interaction between the OsF_6 molecules and the graphite layers. The ratio between the intensities of the $\hat{E}_{2g_2}$ mode and the 1360-cm^{-1} line is usually used in graphite materials to estimate the in-plane crystalline size.[19] However, in stage-1 acceptor GIC's this way of estimating the crystalline size is not correct. The Raman scattering in the blue-green region is resonantly enhanced.[20,21] The enhancements for $q=0$ phonons and for off-zone-center phonons are not the same and may differ from each other by an order of magnitude. Therefore, we can only conclude that the crystalline size in our system is much less than 250 Å.

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