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Lattice stability and limits to charge transfer in intercalated graphite

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It is shown that anodic oxidation of graphite in H_2SO_4 ultimately leads to creation of C–O covalent bonds which act as carrier scattering centers, degrading the metallic behavior of the intercalation compound. This effect sets in at a carrier density corresponding to 0.03–0.05 free holes per carbon atom, thus implying a fundamental limitation to the basal plane conductivity of acceptor compounds. It is argued that a covalent component to the interlayer interaction is, in fact, necessary to stabilize the structure when the density of charged intercalant exceeds a certain limit.

INTRODUCTION

Two broad classes of charge-transfer compounds may be formed by reacting graphite with electron acceptors.[1] Weakly oxidizing species produce intercalation compounds in which the guest-host interaction is mainly ionic and the charge transferred to the carbon layers is delocalized, leading to metallic behavior. Strong oxidizers or fluorinating agents produce covalent insulating solids in which the transferred charge is localized in a C–O or C–F bond and the planar hexagonal array of C atoms is puckered, hence the lamellar structure is destroyed. Several workers have speculated on the possibility of a continuum between these two extremes. Boehm[2] suggested that the formation of the covalent insulator graphite oxide is, in fact, preceded by oxidative intercalation. Starting from the other extreme, Ubbelohde[3,4] and co-workers observed a limiting charge transfer of approximately one electron per 24 C atoms during electrolytic intercalation of graphite in H_2SO_4, and suggested that further oxidation produced alicyclic networks and eventually graphite oxide.

The possible connection between covalent and ionic compounds is relevant to two important issues in intercalated graphite. The first is the optimization of electrical conductivity, particularly Vogel's hypothesis[5] that stronger acids lead to enhanced metallic behavior due to greater fractional charge transfer.[6] Boehm and co-workers[7] have demonstrated the production of C–F bonds under extreme reaction conditions with reagents that normally produce intercalation compounds. Boehm and co-workers[7] and Fischer[8] postulated that very small concentrations of such covalent bonds would act as scattering centers and hence could limit the conductivity. The second issue relates to lattice stability and the limiting charge transfer observed by Ubbelohde. Fischer[8] and Markiewicz[9] have pointed out that neutral molecules play an important role in screening the Coulomb repulsion among intercalant ions within a single layer, since the compensating holes are largely confined to the flanking graphite layers. Ubbelohde's result suggests that a strictly ionic compound can only support a maximum in-plane Coulomb repulsion equivalent to one elementary charge per 24 C atoms, implying that a stage-1 compound of the form C_8X will only be stable if $\frac{2}{3}$ of the X species are neutral (or, equivalently, if unit charge is shared by three molecules). In addition to implying a limiting charge transfer within the ionic regime (and hence a maximum density of delocalized charge on the carbon layers), the stability issue calls into question the ionic salt formulation $C_{12}^{+}MF_6^{-}$ recently proposed for some newly discovered intercalation compounds.[10,11]

Our purpose here is to demonstrate that oxidative intercalation of graphite beyond some limit does indeed produce a reduction in electrical conductivity, and that this reduction is due to the creation of covalent bonds which act as carrier scattering centers. The graphite bisulfate system is particularly convenient for such a study since the charge per C atom is controlled electrochemically[12] by anodic oxidation of a graphite electrode in anhydrous H_2SO_4. In a preliminary report[13] we showed that the conductivity reached a maximum at an oxidation level corresponding to C_{21}^{+}. Here we present data on the temperature dependence of conductivity and magnetoresistance, which clearly show that the decrease in conductivity beyond C_{21}^+ is a mobility effect. Furthermore, x-ray photoelectron spectra in the C 1*s* core-level region show the introduction of C–O bonds at the same charge density. The correlative data presented here as a function of oxidation state thus fully confirm the above hypotheses.

RESULTS

The graphite bisulfate system has been extensively studied in the past.[3,4,12-14] Intercalation is typically monitored by recording the cell potential between the graphite anode and a reference electrode as a function of time at constant current density. For low oxidation levels, steps in the cell potential versus time signal the transition from one stage to another. Here we are concerned with the properties of stage-1 compounds as a function of accumulated charge.

Previous work[13,14] has shown that the first appearance of a pure stage-1 compound corresponds to accumulation of one unit of charge per 27 C atoms, i.e., a formal composition $C_{27}^+HSO_4^- \cdot XH_2SO_4$. The value of X is determined by weight uptake to be ~2.5. The neutral molecules presumably serve to screen the intralayer Coulomb repulsion among HSO_4^- ions. Indeed, in all well characterized acceptor compounds, a large fraction of neutral molecules appear to be incorporated along with the electrically active ionic species.[8,15,16] Increasing the charge density to C_{21}^+ ("overcharging") gives a slight enhancement of the conductivity. This corresponds to conversion of some neutral H_2SO_4 to active HSO_4^- (i.e., a small decrease in X), accompanied by evolution of H^+ which is reduced to H_2 gas at the cathode. Further charging beyond C_{21}^+ induces a precipitous drop in conductivity. This process has been labeled "overoxidation" and continues up to C_{12}^+ at which point the electrolyte decomposes.[13,14] In what follows, we compare the detailed properties of graphite electrodes as a function of oxidation level within the stage-1 regime (i.e., C_{27}^+–C_{12}^+).

Figure 1 shows the temperature dependence of basal conductivity σ_a for normal (C_{27}^+) and overoxidized (C_{12}^+) samples.[17] At C_{12}^+, the compound exhibits typical behavior for a highly metallic stage-1 material. The 300-K value $3\times10^5\ \Omega^{-1}\text{cm}^{-1}$ is comparable to that of "C_8AsF_5,"[18] and the ratio $\sigma_a(80\text{ K})/\sigma_a(300\text{ K})\sim6$ is characteristic of many stage-1 acceptor compounds.[19] The anomaly and hysteresis in $\sigma_a(T)$ at ~200 K is associated with an order-disorder transition of the intercalant layer.[20] Continuing the electrochemical oxidation to C_{12}^+ (overoxidation) leads to a tenfold or more decrease in $\sigma_a(300\text{ K})$ and a flattening of the temperature dependence, as shown in Fig. 1. The anomaly associated with the order-disorder transition is still present, although altered in form, while the overall temperature variation is reduced from $\sigma_a(80\text{ K})/\sigma_a(300\text{ K})=6$ to less than 2. This evolution in $\sigma_a(T)$ between C_{27}^+ and C_{12}^+ is consistent with the introduction of a large, temperature-independent contribution to the resistivity, as would be associated with defect scattering via Matheissen's rule.

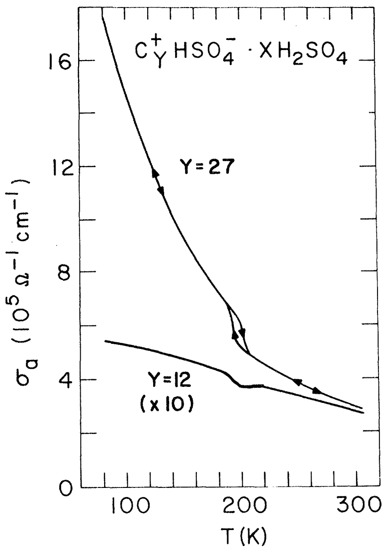

FIG. 1. Temperature dependence of basal plane conductivity σ_a for normal ($Y=27$) and overoxidized ($Y=12$) stage-1 graphite bisulfate. Samples were removed from the electrochemical cell and sealed in Pyrex under inert gas prior to measurement. Data obtained with a rotating sample magnetometer described in Ref. 9. Note that the σ_a scale is amplified 10 times for $Y=12$.

Figure 1 suggests that the conductivity degradation upon overoxidation is a mobility effect rather than a density-of-states effect. This is confirmed by magnetoresistance and reflectance measurements. The magnetoresistance coefficients $\Delta\rho_a/\rho_a$ were measured[17] at 77 K and 3 kG with $\vec{H}\parallel\vec{c}$; for C_{27}^+, $\Delta\rho_a/\rho_a=0.15$, while for C_{12}^+, $\Delta\rho_a/\rho_a$ was immeasurably small. Taking the upper limit at C_{12}^+ as $\Delta\rho_a/\rho_a<0.005$ and assuming $\Delta\rho_a/\rho_a=\mu^2H^2$, where μ is some average mobility, the ratio $\mu(C_{27}^+)/\mu(C_{12}^+)$ is at least a factor of 6, consistent with the relative σ_a values. (Similar experiments on AsF_5 graphite suggest that the relationship between μ and the conductivity mobility is complex, due to a complex Fermi surface.[19]

Figure 2 compares reflectance spectra for normal (C_{27}^+), overcharged (C_{21}^+), and overoxidized material (the same sample was measured versus accumulated charge). At C_{27}^+, the position and shape of the Drude-type plasma edge are compar-

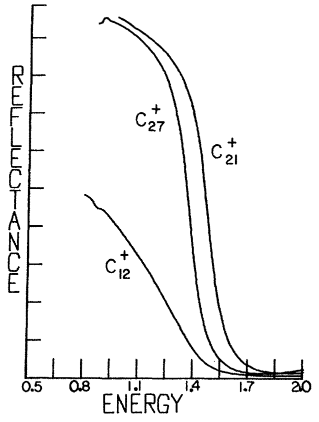

FIG. 2. Normal incidence *in situ* reflectance spectra for normal (C_{27}^+), overcharged (C_{21}^+), and overoxidized (C_{12}^+) stage-1 samples. Absorption by the H_2SO_4 electrolyte and the CCl_4 index-matching liquid affect the data below 0.9 eV (see Ref. 14 for details). The weight uptake is essentially the same for all three samples (Ref. 17), so the variable charge on the carbon implies an electronic rearrangement within the intercalant layer.

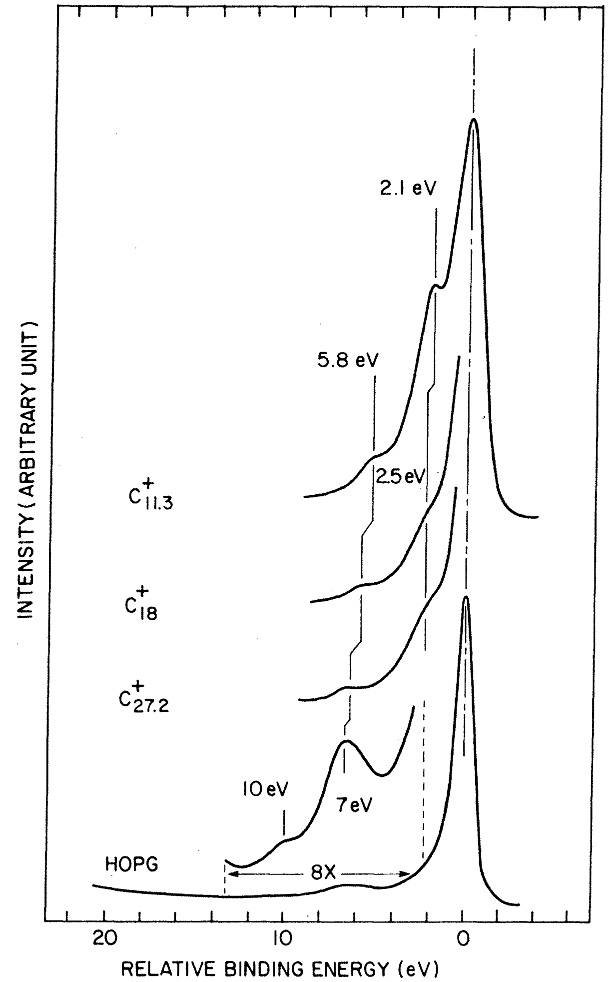

FIG. 3. X-ray photoelectron spectra of the C 1*s* region for several samples are shown. The instrumental resolution is about 1 eV. The spectra are aligned according to the principal maximum and only relative energies are discussed in the text.

able to C_8AsF_5.[21] Overcharging to C_{21}^+ produces a small blue shift, implying slightly higher carrier density. At C_{12}^+ the metallic edge broadens markedly and the low-energy asymptotic value decreases, both of which imply a reduction in carrier scattering time. The location of the minimum does not change, indicating that the additional charge accumulated between C_{21}^+ and C_{12}^+ is localized.

At this point the data provide strong presumptive evidence for the introduction of carrier scattering defects during overoxidation. The nature of these defects is revealed by x-ray photoemission spectra in the region of the carbon 1*s* core level (Fig. 3; experimental details described in Ref. 16). Spectra are shown for normal (C_{27}^+) and overoxidized (C_{11}^+) stage-1 samples and an intermediate case (C_{18}^+) as well as for pure graphite. The spectra are aligned relative to the C 1*s* main peak, the binding energy of which in graphite is 284.4 eV.[22] This procedure is preferred, since the expected chemical shift associated with the transfer of unit charge per 27 C atoms[16] is 0.2 eV, and the differences in absolute binding energy among the spectra of Fig. 3 are too small relative to the reproducibility of the measurement.

The pure graphite spectrum is dominated by the C 1*s* peak associated with sp^2-bonded carbon atoms of graphite. A weaker feature at 7.0 eV is due to a collective oscillation of the π valence electrons, which is excited in conjunction with a C 1*s* photoemission event. The still weaker 10-eV feature is associated with a band-structure effect in pure graphite.[22] The C_{27}^+ intercalation compound shows an appreciable broadening of the C 1*s* peak, as has been observed in other acceptor compounds.[16,22] A very weak, rather broad shoulder near 2.5 eV is also observed. This is possibly attributable to the free-carrier plasmon associated with the delocalized holes in the metallic compound.[23] It is definitely *not* an indication of a new bonding environment of C atoms, since it is also observed for H_2SO_4 simply adsorbed onto the surface of graphite.[23] Also, the π plasmon shifts from 7.0 to 5.8 eV, signalling a reduction in valence bandwidth due to the depression of the Fermi energy associated with the charge transfer via intercalation. The shift of the π-plasmon energy with degree of charge transfer has been observed previously in $FeCl_3$ graphite intercalated compounds (GIC's) using high-energy electron-energyloss spectroscopy.[24] Finally, the overoxidized sample (C_{11}^+) exhibits an additional, strong and rather sharp peak at 2.1 eV relative energy. We attribute this peak to C atoms singly bonded to oxygen atoms (i.e., C–O bonds). This assignment is made on the basis of known binding energies of C–O bonded C atoms in a wide variety of model compounds.[25] Thus the 2.1-eV feature in the C_{11}^+ C 1*s* spectrum is associated with C–O bonds, i.e., carbon atoms in the graphite lattice which have an sp^3 configuration.

DISCUSSION AND CONCLUSIONS

Since the emergence of the 2.1-eV satellite correlated with the decrease in conductivity (Fig. 1) and optical scattering time (Fig. 2), we conclude that C–O bonds are, in fact, responsible for the carrier scattering. Ignoring cross-section effects, the area ratio of the 2.1-eV satellite to the main peak implies a sizable fraction of sp^3 carbons, of the order of 5%. Other information suggests that this is misleading, and that the density of C–O bonds is smaller. First, the (00*l*) x-ray diffractogram does not change appreciably between C_{27}^+ and C_{12}^+, the only observable effect being a reduction in repeat distance from 7.98 to 7.88 Å.[26] Second, assuming that C–O bonds limit the transport mean free path at 300 K, the conductivity reduction implies a "defect density" of only 0.1% of the total carbons (assuming 0.1 μm for the electron-phonon mean free path at C_{27}^+). The discrepancy may be attributable to the fact that the direct attack of the graphite network during overoxidation begins at the sample surface and may be more severe near the surface than deep within the bulk. The transport measurements are thus more bulk sensitive, whereas x-ray photoelectron spectroscopy (XPS) is very surface sensitive.

Qualitative evidence for covalent bonds has been reported in other acceptor compounds, particularly graphite-SbF_5 (Ref. 7) and graphite-KrF_2.[27] In these cases direct fluorination of the hexagonal carbon network is implied. To the best of our knowledge, the present work provides the first direct correlation between sparse covalent bonds and conductivity degradation of an intercalation compound. We suspect that this is a general phenomenon associated with the stability requirements of a quasi-2D ionic system in which the positive charge (the delocalized holes) is ineffective in screening the in-plane Coulomb repulsion among negative charges[8,9] (the intercalant ions). This arises because charges of opposite sign are essentially confined to different layers ~4 Å apart, unlike the situation in normal metals in which the free carriers are delocalized in all three dimensions. The above results imply a generalized limitation to the metallic behavior attainable with ionic salts of graphite. The data in Ref. 13 and Fig. 2 imply a maximum in metallic behavior at a level of oxidation equivalent to $\sim C_{21}^+$, which leads us to question the strictly ionic salt formulation $C_8^+MF_6^-$ (M = As, Os, Ir, ...) proposed by Bartlett *et al.*[10] for a number of novel stage-1 compounds. These latter compounds are all relatively poor conductors [σ/σ (graphite) = 2.2, 1.0, 1.2, respectively] which suggests to us a partial fluorination of the graphite planes. In the context of the hypothesis presented earlier, if no neutral molecules were present, a covalent contribution to the interlayer interaction[18] would be necessary to overcome the large in-plane Coulomb repulsion among unscreened MF_6^- ions. Thompson *et al.*[18] have recently proposed two alternative explanations for the poor conductivity of $C_8^+MF_6^-$ salts, neither of which seem reasonable to us. Their first hypothesis invokes partial localization of the holes on the carbon layers due to the large negative charge density in the flanking intercalant layers. This idea would imply a very poor conductivity for the stage-1 Li compound which can be formulated[18] as $Li^{(1-\epsilon)+}C_6^{(1-\epsilon)-}$, with $\epsilon \lesssim 0.1$, while in fact the conductivity of LiC_6 is nearly the same as the best acceptor values.[29] Their second hypothesis invokes enhanced carrier scattering by the large density per unit area of intercalant ions. This scattering will of course disappear at low temperatures if the intercalant forms an ordered structure; in all known cases, the contribution of this effect is less than 10% rather than a factor of 10.[20] Further experiments are clearly needed to mediate among the various proposals, although to the extent that our overoxidized compound $C_{12}^+HSO_4^- \cdot XH_2SO_4$ resembles "$C_8^+MF_6^-$," we would expect similar phenomena to be operative (i.e., covalent bonds).

The C_{21}^+ limit to ionic salt behavior discussed above is also relevant to the formulation of the stage-1 compound C_8AsF_5 which is an excellent conductor. Bartlett *et al.* originally proposed[10] that the equilibrium $3AsF_5 + 2e^- \rightleftharpoons 2AsF_6^- + AsF_3$ goes far to the right during formation of the compound, leading to a formulation $C_{12}^+AsF_6^- \cdot \frac{1}{2}AsF_3$, which by analogy to the present results would be overoxidized, hence a poor metal. On the other hand, a variety of chemical and physical data[16] are consistent with the formulation $C_{18}^+AsF_6^- \cdot \frac{1}{2}AsF_3 \cdot YAsF_5$ with $Y \sim 1$, in terms of which the high conductivity is more consistent with the C_{21}^+ limit observed in the bisulfate system. It is also found that $Y \rightarrow 0$ with increasing stage index, which can be understood as a relaxation of the need for screening neutrals as the separation between ionic layers increases.[8,9]

We should point out that, due to the long mean free path of graphite and acceptor GIC's very few defects are needed to reduce σ_a (300 K). Covalent bonds (C–O, or C–F) involving 1 atom in 1000 would have a drastic effect on σ_a but would not necessarily show up in chemical or structural data.[11]

A further test of these ideas may come from a detailed comparison of the electronic properties of C_8AsF_5 [fractional ionization 20–30% (Ref. 16)] and $C_8^+AsF_6^-$ (implied ionization 100%).[11] For example, carrier localization in the latter compound should affect the temperature dependence of σ_a. If the stability criteria indeed require covalent bonds beyond a certain fractional ionization, then we have probably already obtained the maximum conductivity achievable with graphite acceptor compounds, i.e., $\frac{1}{2}-\frac{2}{3}$ that of copper. Additional aspects of the XPS spectra of "graphite bisulfate" relevant to the chemical structure of the intercalant layer will be published elsewhere.[23]

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