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Optical and Electrical Properties of Graphite Intercalated with HNO_3 †

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Drude edges are observed in reflectance spectra and compared with the dc transport measurements in the lamellar compounds $C_{6n}HNO_3$ with $n = 1$, 2, and 3. Both measurements confirm the general metallic character of these materials, but the optical data are inconsistent with a simple Drude model. We suggest that this is due either to a complex background dielectric constant or to a multiple-carrier Fermi surface.

Graphite intercalation compounds consist of one or more planes of hexagonally arrayed carbon atoms separated by monolayers of intercalated atoms or molecules.[1] The number of contiguous carbon planes is referred to as the stage of the compound. Many donors (e.g., alkali metals) and acceptors (halogens and acid radicals) have been successfully intercalated. A universal feature of all these compounds is a large increase in the a-axis electrical conductivity, presumably due to an increase in the free carrier density which accompanies the transfer of charge between the graphite and intercalant layers.[2] In this Letter we report the first systematic study of variations in Drude-like reflectance with the intercalant concentration. The optical results confirm the metallic character of these compounds, but a comparison with the dc transport measurements shows that these are not simple Drude metals. Our results are similar to the "transmission windows" reported by Hennig,[3] which could not be analyzed quantitatively because the thickness of the cleaved specimens was unknown.

This Letter deals specifically with the first three stages of the graphite-HNO_3 lamellar compounds. The starting material was highly oriented pyrolytic graphite,[4] in which the spread in c axes of individual crystallites is of order 1 and the crystallite size is of order 1μm. Individual samples for the optical and transport experiments were intercalated using methods developed by Fuzellier.[5] These consist of employing distilled HNO_3 instead of red fuming HNO_3 which allows one to obtain concentrations up to stage 1 without further adjustment of chemistry. The samples were characterized by x-ray, weight-uptake, c-axis dilation, and chemical analyses.[6] The results are all consistent with the chemical formula $C_{6n}HNO_3$, where n denotes the stage of the compound, as previously determined by Ubbelohde.[7] The c axis repeat distance I_c follows the relation $I_c = 7.8 + 3.35(n - 1)$ Å, also in agreement with previous reports.[5,7]

Figure 1 shows the reflectance spectra of freshly cleaved c surfaces for the first three stages. Unpolarized light at near-normal incidence was used (i.e., with the polarization perpendicular to $\vec{c}$). The stage 2 and 3 compounds were measured at room temperature in a flow of N_2 gas, while the stage 1 compound was immersed in carbon tetrachloride at -20°C since it is unstable at higher temperatures.[5] The samples were x-

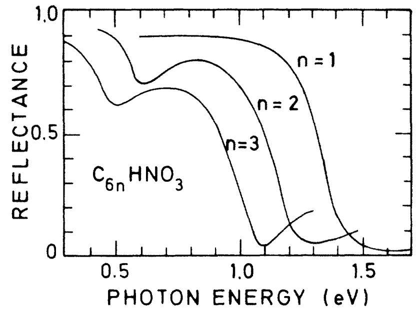

FIG. 1. Reflectance spectra of stage 1, 2, and 3 graphite nitrate intercalation compounds.

rayed before and after the measurement to insure that no changes in composition had occurred.

The dominant effect in all three compounds is a metallic edge, which we associate with the classical plasma of free carriers. The position of this edge shifts monotonically to higher energy with increasing HNO_3 concentration, supporting the idea that charge transfer accompanying intercalation leads to an increase in the free carrier density. The stage 2 and 3 compounds also exhibit broad subsidiary minima at 0.5 and 0.6 eV, respectively. The shape of these curves might suggest a mixture of two stages, but the x-ray analysis gave no evidence of a two-phase system. The low-energy dips are also observed on specimens freshly cleaved in a flow of inert gas. This, plus the fact that the low-energy peak tracks with stage, suggests an intrinsic phenomenon rather than an extrinsic or surface effect. One possibility is the existence of interband transitions in a narrow energy range, by analogy with the reflectance spectrum of Al.[8] Another possible mechanism is an O-H stretching mode internal to the HNO_3 molecule, because such modes are typically found in this spectral region. The stage 1 spectrum could only be measured down to 0.6 eV because of the CCl_4 absorption.

The spectra were analyzed using the Drude expression for the complex dielectric constant. These analyses were performed over a limited range of energy which avoided the extra structure in stages 2 and 3. The results are presented in Table I along with the dc conductivity values measured on standard four-point bridges. Note that σ_{dc} and $\sigma_{opt} = \omega_p^2\tau/4\pi$ differ by as much as a factor of 17, immediately suggesting that the Drude model is too simple to describe the metallic reflectance. This is the main observation of this Letter. The ω_p values in Table I are reasonable; assuming 0.25 free hole per HNO_3 molecule as suggested by Ubbelohde,[7] we calculate effective masses $m^* \sim (0.1-0.2)m_e$, which lie within the range of pure graphite[9] and a free electron $[(0.05-1.0)m_e]$. The scattering times τ_{opt}, obtained by fitting the reflectance data with the simple Drude model, are in the range $(4-6)\times 10^{-15}$ sec, independent of stage, as is apparent from the equal slopes of the plasma edges in Fig. 1. This result is somewhat surprising. Magnetoresistance measurements on stages 2 and 3 indicate mobilities of about 1000 cm^2/V sec for both compounds, which implies that τ_{dc} falls in the range $2.5\times 10^{-14}-5\times 10^{-13}$ sec while m^* lies between values for pure graphite and a free carrier accordingly. Thus, σ_{opt} is less than σ_{dc} by a factor of 5–100. It is clear that τ_{opt} is the source of disagreement between σ_{dc} and σ_{opt}; the low value of σ_{opt} is mainly due to the small τ_{opt} derived from the Drude model.

We feel that the low value of τ_{opt} results from an oversimplified model rather than an experimental limitation. If τ_{opt} were limited by surface contamination, one would expect a greater discrepancy between σ_{opt} and σ_{dc} at higher intercalant concentrations because of the greater reactivity and instability of the saturated compounds. Table I indicates the opposite behavior; σ_{opt} and σ_{dc} converge as n approaches 1.

Improved agreement between optical and transport results can be obtained by generalizing the optical model. A frequency-dependent τ could in principle improve the agreement between σ_{opt} and σ_{dc}; however, this is normally a small correction in simple metals and probably cannot account for the factor-of-17 discrepancy at stage 3.

A possible explanation for the low value of τ_{opt} may be the existence of a weak continuum of interband transitions in the region of the reflectance edge, the effect of which is to make ϵ_0 complex. We note first that in pure graphite $\epsilon \cong 5 + i10$ near 1 eV,[10] the interband strength coming from narrow overlapping bands near the zone edges.[11] The low interband threshold obscures the screened Drude edge expected at 0.5 eV in pure graphite. The observation of edges in the intercalation compounds indicates that the inter-

TABLE I. Drude parameters and dc conductivity of stage 1, 2, and 3 compounds.

Stage	ω_p (eV)	ϵ_0	τ_{opt} (10^{-15} sec)	σ_{opt} ($m\Omega^{-1}$ cm^{-1})	σ_{dc} ($m\Omega^{-1}$ cm^{-1})	σ_{dc}/σ_{opt}
3	2.8	10	5 ± 1	8	140 ± 20	17
2	4.3	12	5 ± 1	16	155 ± 15	10
1	5.5	15	5 ± 1	35	~ 180	5

band strength near 1 eV is greatly reduced, which in very dilute compounds can be understood in terms of a downward shift of E_F out of the region of overlapping bands such that the interband threshold increases greatly. The Drude fits to the stage 3 curve gave $\epsilon_0 = 10$. An equally good fit can be obtained with $\epsilon_0 = 10 + i1$, with the result that τ_{opt} is increased by a factor of 4. Thus the large difference between σ_{opt} and σ_{dc} at $n = 3$ and the convergence as n proceeds through 2 and 1 can be explained by a featureless residual interband strength near the reflectance minimum which decreases in magnitude as n approaches 1. The resolution of this question must await an experiment which yields ϵ_1 and ϵ_2 independently.

A second possibility is suggested by the extremely small Hall coefficient in the stage 1 donor compound C_8K,[12] which strongly implies a complex Fermi surface with comparable densities of electrons and holes.[13] A two-carrier Fermi surface would completely invalidate the Drude analysis of the optical data presented in Table I.

The increase in ϵ_0 with decreasing stage implies a shift in the oscillator strength at $\omega > \omega_p / \sqrt{\epsilon_0}$ from high to low ω with increasing HNO_3 concentration. For example, carbon-HNO_3 bonding would be expected to influence the bound π-electron resonance at 7 eV.[10] We are planning to explore this effect with uv reflectance.

In a previous work,[14] we assumed the applicability of the simple Drude model to predict σ_{dc} from ω_p and τ_{opt} in a new compound, graphite intercalated with $SbF_5 + HF$. The predicted σ_{dc} was comparable to that of copper. Having shown above that the simple Drude model does not necessarily apply, there is no longer any basis for that prediction. In fact, preliminary results by Thompson, Falardeau, and Hanlon[15] show that σ_{dc} for this new compound is $\sim\frac{1}{3}$ that of copper, comparable to the HNO_3 compounds described here.

In summary, the reflectance spectra confirm the general metallic character of the graphite compounds, but σ_{opt} and σ_{dc} cannot be reconciled within a simple Drude model. This is in contrast to the situation found in other synthetic metals such as $(SN)_x$[16] and tetrathiafulvalene tetracyanoquinodimethane[17] (TTF-TCNQ) in which (at least at room temperature) σ_{opt} and σ_{dc} are in reasonable agreement. The Drude analysis yields reasonable ω_p values, but $\tau_{opt} \ll \tau_{dc}$. We find that ω_p increases with HNO_3 concentration as expected, the quantitative behavior suggesting that either m^* or the fraction of a free hole per HNO_3 molecule varies with stage. Several differences are evident between the compounds and the parent graphite. The effective masses appear to be somewhat larger, although not greatly so. The dc scattering times are reduced by at least a factor of 10. Given the possibility of multiple carrier groups, the reported quantities for these parameters may have to be considered "effective" values. The interband-transition strength in the range 0–1 eV is greatly reduced, implying either a totally new band structure or a shift in Fermi energy within the graphite picture. The latter view is the basis of a dilute-limit approach[18] which is expected to be applicable only to compounds with $n \geqslant 5$. We do not expect a rigid-band model to apply to the results presented here. The difference between σ_{opt} and σ_{dc} appears to be intrinsic and may be due either to interband transitions overlapping the Drude edge or to a multiple-carrier Fermi surface.

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Carrier-Concentration-Dependent Phase Transition in SnTe

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The transition temperature T_c of the displacive phase transition in SnTe as a function of the carrier concentration p^* is determined by measurements of the resistance anomaly. The transition temperature T_c decreases gradually with increasing p^* and vanishes at $p^* \sim 1.3\times10^{21}$ cm^{-3}. The results are explained by the electron–TO-phonon interaction model with an optical-deformation-potential constant of 10 eV.

The displacive phase transition in SnTe at low temperatures has been studied by many workers using various experimental methods.[1-5] One of the most interesting features of this phase transition is that it occurs in diatomic narrow-gap semiconductors. This phase transition may be understood with the aid of Kristoffel and Konsin's theory of ferroelectric phase transition based on electron–TO-phonon interaction.[6] The transition temperature T_c, determined by x-ray diffraction, Raman scattering, and neutron scattering, as a function of the nominal carrier concentration of the samples, decreases abruptly at around $p^* \sim 1.5\times10^{20}$ cm^{-3}.[5] Recently, it was found that the electrical resistivity shows an anomalous increase near the transition temperature.[7] The anomalous increase of the resistivity was understood in terms of increasing carrier scattering by the soft TO phonon in the vicinity of T_c determined by the neutron Bragg reflection in the same crystal.[5] This implies that the electron–TO-phonon interaction affects the phase transition.

In order to clarify the role of the electron–TO-phonon interaction in the phase-transition mechanism, T_c was obtained systematically as a function of the carrier concentration. Measurements of the electrical resistivity and Hall coefficient as functions of temperature were made for p-type SnTe single crystals with carrier concentrations of $(1.2-7.7)\times10^{20}$ cm^{-3} at 77 K. Samples with lower carrier concentrations were prepared from solution-grown crystals while those with higher carrier concentration were cut from horizontal Bridgman-grown crystals. Examples of resistivity-versus-temperature curves are shown for the samples with various carrier concentrations in Fig. 1. Each curve has a kink whose position shifts toward the lower-temperature side as carrier concentration increases. The transition temperatures T_c determined from the temperature of the kink are plotted versus the carrier concentration in Fig. 2. Results reported earlier[2-5] are also shown in the same figure.

In order to gain an understanding of the carrier concentration dependence of T_c, we applied the same electron–TO-phonon interaction model that provided a good understanding of the resistivity anomaly due to the phase transition.[7] The TO phonon frequency is reduced by the electron–TO-phonon interaction and the lattice tends to be unstable. This reduction of the TO phonon frequency becomes small when carrier concentration increases, and consequently T_c decreases. Under the assumption of the same parabolic dispersion for conduction and valence bands near the band edges, the TO phonon frequency renormalized with the electron–TO-phonon interaction can be expressed as

$$\omega_{\mathrm{TO}}^{*2} = \hat{\omega}_{\mathrm{TO}}^{2} + \frac{4g}{(2\pi)^3}\left(\frac{\hbar D^2}{2MNa^2}\right)\int_0^{E_{\mathrm{F}}}\frac{\rho(E)\,dE}{E_G+2E}, \quad (1)$$