Fermi-Level Lowering and the Core Exciton Spectrum of Intercalated Graphite

Eugene J. Mele and John J. Ritsko
Xerox Webster Research Center, Webster, New York 14580

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The lowering of the Fermi energy in stage-1 $FeCl_3$-intercalated graphite is directly measured in the spectrum of electronic excitations from carbon 1*s* core states to empty carbon 2*p* states which appear after intercalation. The shape of the core exciton spectrum is related to the initial distribution of empty states in a formulation of the core exciton problem which includes the effect of electronic relaxation near the core hole.

In spite of great current interest in the properties of intercalated graphites[1-4] and a long history of studies of these materials,[3] detailed microscopic data describing the electronic structure of these systems are scarce. Until now, physical quantities such as the exact position of the Fermi level, have only been indirectly estimated from experimental studies of intercalated systems.[1] In this Letter we report the first direct measurement of the distribution of previously occupied carbon 2*p* states which are depopulated when graphite reacts with an acceptor intercalant. The difference in the position of the Fermi level before and after intercalation is given by the width of this distribution. This information was obtained for stage-1 $FeCl_3$-intercalated graphite from an analysis of the spectrum of electronic excitations from the carbon 1*s* core levels to empty carbon 2*p* states near the Fermi energy. Noting that excitonic effects severely modify the qualitative features of the absorption edge in graphite, our analysis includes a formulation of the core exciton problem which includes the effect of electronic relaxation near the core hole. This theory provides the first quantitative description of the core-electron absorption-edge line shape in graphite and allows a direct determination of Fermi-energy lowering in intercalated graphite.

In the experiment, energy-loss spectra of 80-keV electrons transmitted through thin (~1000-Å) samples were measured with a resolution of 0.11 eV (full width at half maximum). Electrons were collected at zero scattering angle ($\pm 2\times10^{-4}$ rad). In order to achieve ~1% statistical accuracy, data for each material were taken in multiple runs on several samples for a total period of ~7 h per material with a beam current of 3.3×10^{-9} A. Samples of stage-1 $FeCl_3$-intercalated graphite were carefully prepared and characterized by standard techniques.[5]

Electron-energy-loss spectra for pristine and stage-1 $FeCl_3$-intercalated graphite are shown in Fig. 1. The absorption edge in pure graphite is characterized by a broad, nearly symmetric peak at 285.35 ± 0.05 eV centered approximately 1 eV above threshold. In the intercalated material a peak of similar shape is observed at 285.55 ± 0.05 eV, accompanied by new structure between 283.2 and 284.2 eV which can only be due to the excitation of carbon 1*s* electrons into *p*-like electronic states which have been emptied by charge transfer to the intercalant. The small shift of the strong peak to higher energy in the intercalated material is most likely due to an increase of the carbon 1*s* binding energy caused by the greater net charge per carbon atom. While the width of the new peak at threshold is clearly a measure of how much the Fermi level has been lowered on intercalation, a precise measurement of this quantity is not possible unless an accurate description of the absorption line shape

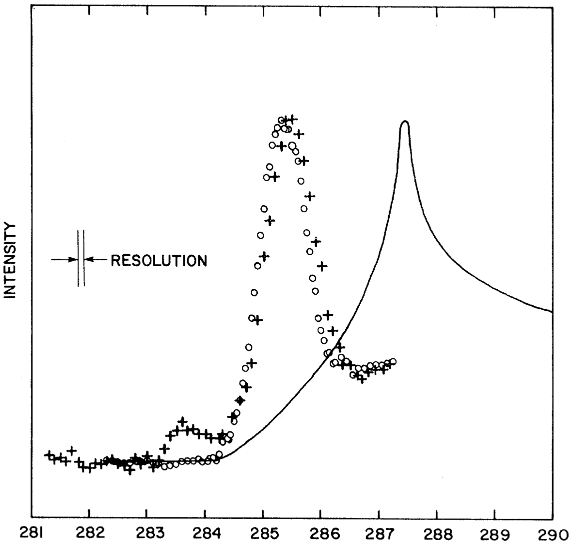

FIG. 1. Experimental electron-energy-loss spectra: graphite (circles), stage-1 $FeCl_3$-intercalated graphite (crosses); graphite density of empty states (solid curve).

is available. A first approximation to the spectral shape is the ground-state density of empty carbon p states. But as shown in Fig. 1 this provides a poor description of the experimental data. Such lack of agreement between the one-electron ground-state density and the measured core absorption spectra is a general feature common to similar core excitation studies in metals,[6,7] semiconductors,[8,9] and insulators.[10] These discrepancies follow from the strong interaction of the final-state electrons with the core hole left behind. Thus a more realistic theory of the absorption spectra must incorporate the electron-hole interaction into a description of the final states of these systems.

For studies involving atoms or small molecules, this relaxation of the final state can be easily treated by calculating separately the initial and final states from self-consistent potentials defined by their respective electronic configurations.[10] In the present work, we incorporate into our description of the excited states of graphite the principal features of such a self-consistent relaxation calculation. We consider a single graphite plane in which a 1s core electron is missing on an atom labeled α, and assume that the electrons in this neutral solid have relaxed self-consistently in the presence of the core hole. This relaxation screens the hole on the αth site canceling the long-range Coulomb tail. To describe the π bands of this material we employ a localized-orbital model and assign to each site a p orbital directed along the c axis. The Hamiltonian includes diagonal and nearest-neighbor interactions. For the *unexcited* solid such an approximation yields an excellent description of the π-band structure and the associated dielectric response functions.[11-13] For the excited solid we distinguish the diagonal matric element on the αth site and nearest-neighbor interaction terms coupling to the αth site from all the other interactions in the solid which are assumed to retain their bulk values. This Slater-Koster model correctly destroys the translational symmetry of the graphite lattice, and includes the largest effect of the new "crystal" potential.

To solve for the density of states of this nonperiodic structure, we employ a scattering-theory formalism[14] recently applied to defect studies in semiconductors.[15,16] In this formalism, we first construct the single-particle Green's function, for the unperturbed solid, $\tilde{G}^0(E)$. Denoting the difference between the Hamiltonians describing the ground-state and excited solid by H', we can obtain the Green's function for the nonperiodic structure, $\tilde{G}(E)$, from the Dyson equation:

$$\tilde{G}(E)=\tilde{G}^0(E)+\tilde{G}^0(E)H'\tilde{G}(E). \qquad (1)$$

The finite range of H' allows a convenient exact solution for $\tilde{G}(E)$. Finally, the cross section for a transition from the core state on site α to these relaxed final states is proportional to the local density of relaxed empty states on the αth site, $\pi^{-1}\mathrm{Im}\tilde{G}_{\alpha\alpha}(E)$. This approach is similar to previous scattering-theory formulations of various exciton problems.[17-19] We retain two adjustable parameters in the theory, namely the diagonal matrix element of the perturbation Hamiltonian on the site α, labeled ΔE, and the off-diagonal matrix element of this Hamiltonian coupling α to its nearest neighbors, labeled ΔV_π. ΔE and ΔV_π are chosen to provide a good description of the core exciton line shape in pure graphite, and are then used to calculate the line shape of the intercalated material.

Our results for the core exciton line shape in pure graphite are shown in Fig. 2. The dashed curve represents the ground-state density of states of the antibonding π band and the open circles are the experimental energy-loss spectrum. The solid curves represent the local densities of final states on the excited atom for two separate relaxation models. Theoretical curves include a Lorentzian broadening with $\Gamma = 0.075$ eV to ac-

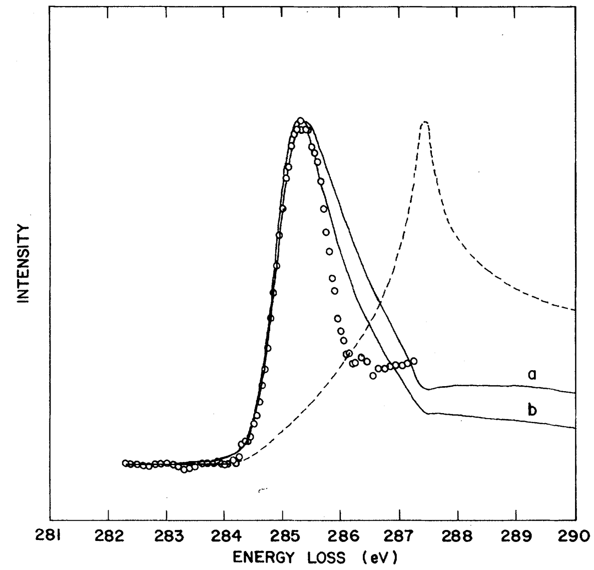

FIG. 2. Graphite: Energy-loss data (circles), ground-state density of empty states (dashed curve), and theoretical density of final states (solid curves).

count for the finite lifetime of the core hole. For the solid curve a, ΔE is taken to be − 6 eV and $\Delta V_\pi = -0.25$ eV, while the values of these quantities for the curve labeled b are − 3 and + 0.3 eV, respectively. As is apparent in the figure, the principal effects of both relaxation models are to shift the peak of the crystalline density of states to lower energy and to round off and broaden this peak. The shifted, broadened, relaxed peak is due to electronic states which are Bloch-like far from the excited atom but are resonantly enhanced in the vicinity of the core hole. The results of Fig. 2 show that the differences in spectral shape between the measured core excitation spectrum and the one-electron density of empty states are correctly described by the localized relaxation model. In fact, the theory predicts that the logarithmic singularity in the original density of states should be replaced by a kink in the tail of the relaxed spectrum, a feature which also occurs in the experimental data at about 286.6 eV.

The two parameters, ΔE and ΔV_π, which emerge from the analysis provide two important results. First, the magnitude of ΔE is typical of binding energies of very localized Frenkel excitons in solids.[10] We therefore identify the core exciton in graphite as a Frenkel-like resonance. This is confirmed by density-of-states calculations on neighboring atoms which show that the final state is enhanced on the absorbing site and a few nearest neighbors. Second, although ΔE and ΔV_π are surely the largest perturbations in the solid due to the core hole, we find in practive that ΔV_π is quite small with respect to ΔE. Therefore our initial approximation of ignoring even smaller higher-order terms in the perturbation Hamiltonian appears to be well justified.

The results for the core exciton spectrum of stage-1 $FeCl_3$-intercalated graphite are shown in Fig. 3. The convention is the same as in Fig. 2. The relaxation models provide an excellent description of the energy-loss spectrum. The theoretical curves shown in Fig. 3 correspond to a lowering of the Fermi energy by 0.9 eV in the intercalated material, and correctly predict the position, magnitude, and shape of the absorption edge. It is interesting to note that while a complete theoretical calculation was necessary to describe the entire absorption line shape, the lowering of the Fermi level can be obtained directly from the experimental data as the width of the small peak. However, this result cannot be reached *a priori*. If we assume that the carbon π bands are unperturbed in the intercalated material, a movement of the Fermi energy of 0.9 ± 0.1 eV corresponds to a charge transfer of $0.011e^-$ to $0.018e^-$ per carbon atom to the intercalant, and a density of states at the new Fermi energy of 0.031 to 0.040 electrons/eV carbon atom. This is an extremely small charge exchange which is consistent with the rigid-band approximation. Further evidence that the π bands are only weakly perturbed in this compound was provided by studies of the π-plasmon dispersion and an accurate measurement of the interband transition at the Q point of the Brillouin zone.[5,13]

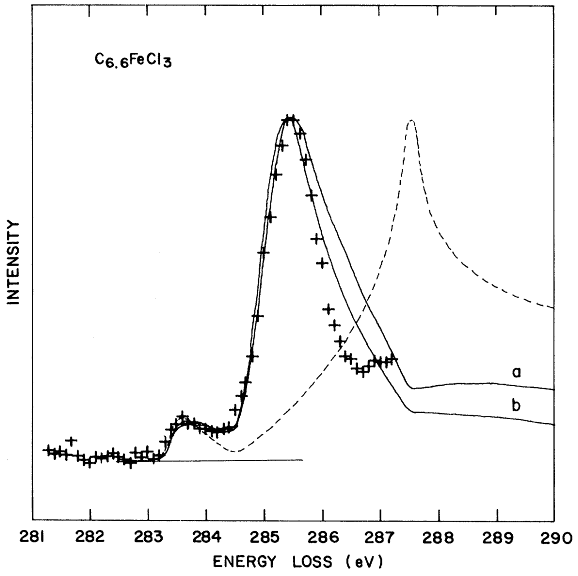

FIG. 3. Stage-1 $FeCl_3$-intercalated graphite: experiment (crosses), ground-state empty states (dashed curve), theoretical density of final states (solid curves).

The theoretical methods we have used are completely general and can be applied to many outstanding problems concerning precise calculations of soft-x-ray absorption-edge line shapes. The technique of measuring electronic excitations from carbon 1s core states to empty carbon p states can be applied to all intercalated graphite compounds and the distribution of carbon 2p states and changes in the Fermi level can now be measured with an accuracy limited only by instrumental resolution.

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Observation of a Continuum in Enhanced Raman Scattering from a Metal-Solution Interface

Ronald L. Birke and John R. Lombardi
Department of Chemistry, City College of the City University of New York, New York, New York 10031

and

Joel I. Gersten[(a)]
Department of Physics, City College of the City University of New York, New York, New York 10031

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A background continuum in the Raman spectrum of adsorbed molecules at a silver-electrolyte interface is observed experimentally. This background continuum is potential dependent on the Stokes and anti-Strokes of the spectrum and fits a Fermi distribution function on the anti-Stokes side of the spectrum. The continuum is interpreted in terms of radiative recombination of adsorbed molecular ions produced by photoionization.

Raman scattering from molecules adsorbed on the surfaces of solids has been the focus of considerable interest lately.[1] Light scattered from adsorbed molecules at a metal-solution interface has been observed to be several orders of magnitude more intense than would be expected on the basis of extrapolations from the liquid or gas phase. Observations of an apparent monolayer of adsorbed CN$^-$ on Ag at the silver-air interface also show intense Raman spectra.[2] A strong background was reported which was not due to Rayleigh-scattered light.[2] We have also observed this strong background continuum scattering at the Ag-solution interface. The nature of this background continuum scattering on the Stokes and anti-Stokes side of the spectrum is the subject of this Letter.

The experiments were performed with a Coherent Radiation Inc. model 52 argon-ion laser operating at 2.5 W output power (distributed over all lines). The 4880-Å line was isolated by an interference filter which does not completely filter out extraneous laser lines near 4880 Å; however, these lines do not seriously interfere with the spectrum. The filter is effective in blocking fluorescence from the laser plasma tube. The laser is focused by a 2-in.-focal-length lens onto the electrode with a spot size of approximately 1 mm. We estimate that as a result of losses in the filter and other optical components the effective power at the electrode is less than 200 mW. The scattered radiation was analyzed using a Spex model 1401 double spectrometer with slits at 100 μm giving a resolution of 2 cm^{-1}. Intensity was measured using a cooled photomultiplier and standard photon-counting electronics supplied with