Plasmon Spectra of Ferric-Chloride-Intercalated Graphite

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High-resolution electron energy-loss spectra show unexpected features of electronic excitations in stage-1 $FeCl_3$-intercalated graphite. A sharp 1-eV plasmon surprisingly exhibits positive quadratic dispersion and damping characteristic of a free three-dimensional electron gas. However, the dispersion coefficient is very large and the intensity falls unusually sharply with increasing momentum, indicating the likelihood of strong band-structure effects. An intense 5.9-eV energy loss is identified with a shifted π plasmon in graphite consistent with only weakly perturbed carbon π bands.

Because of their high electrical conductivity and novel crystal structure, graphite intercalation compounds are presently the object of many investigations.[1] Of central importance in these studies is the nature of the electron gas responsible for the high conductivity. Optical reflectivity studies of low-stage intercalation compounds invariably show a sharp dip in the range 1–3 eV similar to a Drude or plasma edge in simple metals.[2] In this work, we report the energy and momentum (q) dependence of plasmons associated with Drude edges in stage-1 ferric-chloride–intercalated graphite. The results show that excitation of the conduction electrons exhibits features usually associated with a free three-dimensional electron gas, namely, positive quadratic plasmon dispersion and damping. However, simple free-electron–gas models fail to explain a most unusual and somewhat dramatic fall in plasmon intensity with increasing q. This anomalous behavior points to the likelihood of a strong influence in the excitation spectrum of band-structure effects. In addition, the range of previous optical studies is extended to 10 eV, and a plasmon at 5.9 eV, reported here for the first time, provides evidence that the π-band structure is only weakly perturbed in this stage-1 compound.

In the experiment, energy-loss spectra of 80-keV electrons transmitted through thin samples were measured as a function of momentum transfer (q) with an energy resolution of 0.11 eV full width at half maximum (FWHM) and a momentum resolution of 0.055 $Å^{-1}$ FWHM. Slabs of highly oriented monochromator-grade pyrolytic graphite (HOPG) $1.0\times0.4\times0.025$ cm^3 were intercalated with $FeCl_3$ by heating the graphite at 320°C for 2–5 day in an inverted U tube with the ferric chloride at 300°C. Anhydrous $FeCl_3$ had previously been distilled into one end of the U tube which was outgassed and then sealed at a pressure of 5×10^{-6} Torr. Samples increased in weight by a factor of 2.3–2.6 on intercalation. X-ray diffraction patterns showed the material to consist primarily of stage-1 $FeCl_3$-intercalated graphite (C-C interplanar distance 9.4 Å) with a small component of unintercalated material similar to previous results.[3] $FeCl_3$-intercalated graphite was chosen for its stability in air, vacuum, and a variety of solvents.[3] Thin samples were prepared by adhesive tape cleaving followed by dissolving the adhesive in chloroform.

Typical energy-loss spectra are shown in Fig. 1. Two prominent features dominate the low-q (0.1 $Å^{-1}$) spectrum: a sharp peak at 1.1 eV (0.3

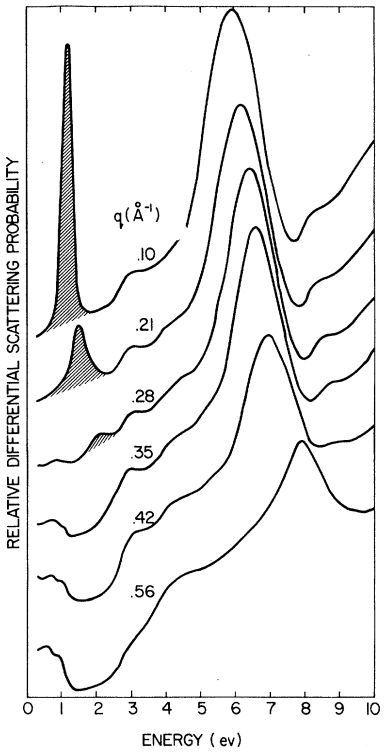

FIG. 1. Momentum dependence of electron energy-loss probability measured in stage-1 $FeCl_3$-intercalated graphite. $\vec{q}$ parallel to graphite planes.

eV wide) and a broader loss at 5.9 eV. The former would be associated with a Drude reflectivity edge as is seen in all low-stage intercalated graphite compounds[1,2] while the latter is quite similar to a plasmon excitation associated with a reflectivity edge in crystalline graphite at 7.0 eV.[4,5] Furthermore, we studied cleaved HOPG and found excellent agreement with q-dependent crystalline-graphite measurements.[4] At small q the only structure in HOPG in the 0–10-eV region is a low steplike threshold at ~ 1 eV (due to interband transitions) and the 7-eV plasmon. The sharp 1-eV peak is a consequence of $FeCl_3$ intercalation. Charge is transferred from the carbon π band reducing some iron.[6] Intraband excitations in the partly filled π band give rise to metallic conductivity and the 1-eV plasmon loss.

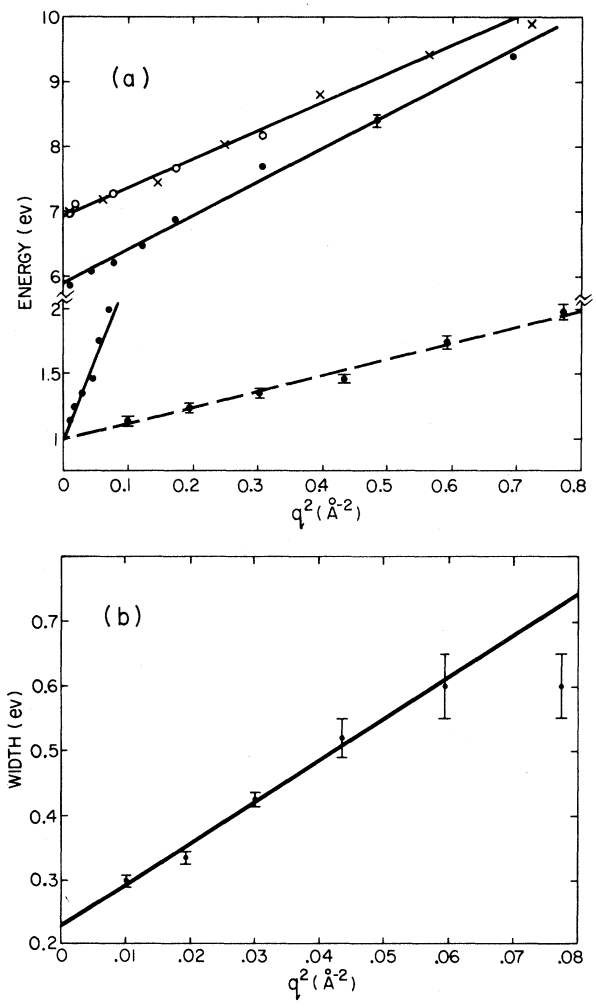

FIG. 2. (a) Plasmon dispersion: solid dots, intercalated graphite; open circles, HOPG; crosses, crystalline graphite (Ref. 4); the dashed line is through 1-eV plasmon data redrawn on 10× expanded scale. (b) FWHM of 1-eV plasmon.

The dispersion and damping (width) of a plasmon contain fundamental information about electrons taking part in the plasma oscillation. The momentum dependence of the plasmon energy (E_p) of a free-electron gas is[7]

$$E_p = E_{p0} + \alpha(\hbar^2/m)q^2. \quad (1)$$

Here m is the free-electron mass and if v is the velocity, $\alpha = mv^2/2E_{p0}$. E_{p0} is the plasmon energy at $q = 0$. For Li, Na, Al, and other simple metals $\alpha = 0.26$–0.42.[7] As shown in Fig. 2(a), the 1-eV plasmon disperses quadratically, but $\alpha = 1.65$. Data on an expanded q scale are also shown. A large α is due to the large average energy of the plasma electrons relative to the plasmon energy. The width W of a plasmon is inversely proportional to the electron-lattice scattering time τ and is a measure of the damping of the plasma resonance.[7] In free-electron metals, W increases quadratically with q in a relation similar to Eq. (1).[8] This quadratic dependence is also found for the 1-eV plasmon as seen in Fig. 2(b). The slope of the line is 6.4 eV Å^{-2}.

As shown in Fig. 1, the most dramatic feature of the momentum-dependent energy-loss spectra is the rapid loss of strength of the 1-eV plasmon with increasing q. The peak height falls as q^{-4} as shown in Fig. 3. In simple metals, the plasmon peak height falls nearly as q^{-2} for the small momenta measured here,[7] and most other features in our spectra, including the height of the π plasmon, show roughly a q^{-2} dependence. Also given in Fig. 3 is a plot of the integrated strength which is defined as an integral over the energy times the intensity. We have performed a calculation of the momentum-dependent dielectric response of a three-dimensional electron gas with a two-dimensional Fermi surface in the random-phase approximation to see if the q dependence of the intensity could be a two-dimensional effect. The calculation parallels that of Stern for an isolated two-dimensional electron gas.[9] The results show that quadratic dispersion is to be expected. However, the observed q^{-4} dependence of the peak height cannot be accounted for and is not due to reduced dimensionality. The q dependence of the intensity cannot be explained by simple free-electron–gas models and a calculation which takes account of the band structure of the intercalated material is, presumably, necessary to explain this effect.

The 5.9-eV peak in $FeCl_3$-intercalated graphite

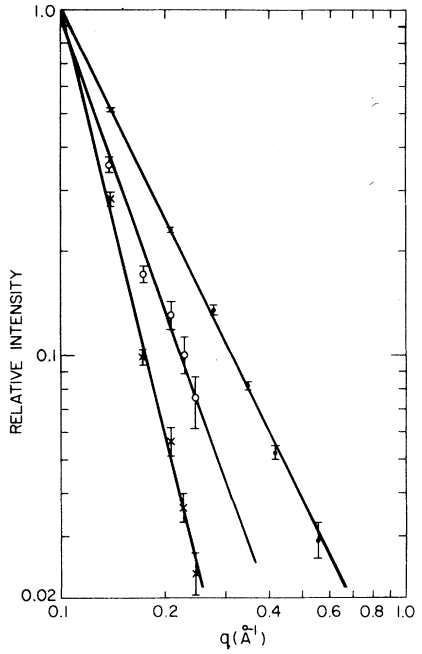

FIG. 3. Momentum dependence of plasmon intensity: solid circles, 5.9-eV plasmon peak height $\propto q^{-2.06}$; crosses, 1-eV plasmon peak height $\propto q^{-4.1}$; open circles, 1-eV plasmon integrated strength $\propto q^{-2.8}$.

may be identified with a shifted 7.0-eV plasmon in pristine graphite. These excitations have similar dispersion as shown in Fig. 2(a). The dispersion follows Eq. (1) with $\alpha = 0.58$ for graphite and 0.68 for the intercalated compound. A somewhat larger α is consistent with lower E_{p0} if the simple free-electron model embodied in Eq. (1) is assumed. Moreover, as shown in Fig. 3, the intensity falls as q^{-2} identical to the 7-eV plasmon in graphite.[4] In addition, the width of both of these excitations is nearly independent of q over the region studied here.

In crystalline graphite, the 7.0-eV plasmon occurs after the exhaustion of the oscillator strength of the $\pi \rightarrow \pi^*$ interband transitions and is essentially a response to these excitations.[5] A peak in the imaginary part of the dielectric response function (ϵ_2) at 4.8 eV drives the real part (ϵ_1) through zero. ϵ_1 then recrosses zero near 7 eV causing the observed plasmon.[5] The peak in ϵ_2 is associated with interband transitions at the M point of the Brillouin zone.[10] The fact that a strong plasmon is observed at 5.9 eV in the intercalated material indicates that the π-band structure cannot be grossly perturbed in this stage-1 compound. In fact, since charge is removed from the carbon planes, the π bands should narrow as a result of greater attraction to the carbon cores, reducing the gap at the M point and lowering the π-plasmon energy. Charge transfer will also reduce the total oscillator strength of $\pi \rightarrow \pi^*$ transitions by eliminating part of the low-energy joint density of states.[4] This effect will tend to lower the π-plasmon energy further. Accurate band calculations to substantiate these notions for $FeCl_3$-intercalated graphite have not been done. However, in the donor compound C_6Li (where band broadening is expected) the π band between Γ and K expands from 7 to 8 eV but is otherwise merely folded into the new Brillouin zone.[10,11]

Additional information about the electronic structure of the intercalated material can be gained from the weaker dispersionless structure shown in Fig. 1. The absorption from 2.5 to 3 eV is due to local excitations in $FeCl_3$.[12] This peak is indicative of Fe^{+3} since $FeCl_2$ (which has a similar crystal structure) absorbs only weakly below 5.7 eV.[13] Thus the degree of charge transfer per intercalant molecule, f, must be less than 1. This is consistent with Mössbauer measurements which show[6] $f = 0.05$ and with Hall-effect measurements which yield $f = 0.25$.[14] However, the present spectra also present evidence for a considerable amount of Fe^{+2}. This is indicated by the doublet at 0.8 and 1.0 eV seen in large-q spectra whose intensity is measured to be q independent. This structure coincides with $d \rightarrow d$ transitions ($t_{2g} \rightarrow e_g$) measured in $FeCl_2$ which show a Jahn-Teller splitting with peaks at 0.94 and 0.79 eV.[15] The intensity is q independent because $d \rightarrow d$ transitions are dipole forbidden and are seen in high-q energy-loss spectra because of quadrupole matrix elements which yield a q-independent energy-loss probability.[16] The peak at 8.2 eV is also seen in $FeCl_2$.[13] However, a quantitative measure of the relative amount of Fe^{+2} cannot be made since the strength of $FeCl_3$ excitations is not known.

Further information about the degree of charge transfer and the band structure of the intercalated compound can be inferred from the sharp plasma loss at 1 eV in the $q = 0.1$ Å^{-1} spectrum. This sharp loss indicates a small value for ϵ_2 at 1 eV since the width of a plasmon is proportional to ϵ_2, and the peak height proportional to $1/\epsilon_2$.[7] For $\pi \rightarrow \pi^*$ interband transitions in crystalline graphite $\epsilon_2 \gtrsim 10$ from threshold to ~5 eV.[4] Such a large value of ϵ_2 would completely damp the plasmon. Thus we must conclude that the interband threshold is greater than 1 eV. To test the implications

of this requirement for the degree of charge transfer, we computed the density of states near the Fermi level with a simple tight-binding model of the π band fitted to an accurate band-structure calculation.[10] Assuming a formula C_6FeCl_3 (Ref. 3) and $f = 0.05$ (Ref. 6) we find the Fermi level is lowered by 0.5 eV and the interband transition gap is 1.0 eV at $q = 0$. The gap is very sensitive to the degree of charge transfer since the density of states is so low near the Fermi level. For $f = 0.10$ the gap is 1.4 eV. Thus $0.05 < f < 1.0$ is consistent with the narrow width of the 1-eV plasmon and the $FeCl_3$ excitation at 3 eV.

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Raman Scattering from Plasmons in Photoexcited GaP

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The plasmon modes of the electron-hole plasma in GaP are investigated by pulsed Raman scattering. The two branches of the coupled plasmon-phonon modes are undamped and are observed over a wide energy range, depending on the excitation density. From this variation it is deduced that the density of electron-hole pairs varies in the range of $(1-4) \times 10^{18}\,cm^{-3}$.

Raman scattering from plasmons has been observed in several doped semiconductors.[1] The experimental observations which were amenable to a full analysis were those of a single-component plasma (electrons in a single-valley conduction band) with negligible damping.[2,3] The great interest in electron-hole liquid (EHL) in photoexcited semiconductors suggests the possibility of using Raman scattering as a means of studying plasmons in such systems.

In this Letter we report the results of a study of Raman scattering from plasmon-phonon coupled modes in pulse-photoexcited undoped GaP. These results constitute the first observation of scattering from a two-component plasma and, in addition, allow a direct determination of the electron-hole density. This method is more sensitive than the conventional line-shape fitting of the electron-hole–plasma (EHP) radiative-recombination spectrum (in the case of GaP). Therefore, it is found that the density of electron-hole pairs is slightly dependent on the excitation intensity.

Single crystals of undoped GaP were excited by a pulsed dye laser pumped with a nitrogen laser. The peak power of the dye laser was 5–10 kW and the excitation intensity at the crystal was about 1 MW/cm^2. The laser pulse width was 2 nsec in the green and 4 nsec in the blue with a