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Valence- and core-electronic excitations in potassium-intercalated graphite

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The valence- and core-electronic excitations of states 1—3 potassium-intercalated graphite have been measured with high-resolution (0.1 eV) electron-energy-loss spectroscopy. Contrary to previous measurements, strong dispersion was observed for intraband plasmons. In addition, the momentum dependence of the spectrum of single-particle intraband excitations was measured for the first time in these materials. Kramers-Kronig analysis of energy-loss spectra yielded the dielectric functions for KC_8 and KC_{24}. Interband transitions at the *M* point of pristine graphite which occur at 4.3 eV are essentially unchanged in KC_{24} but are shifted to 4.0 eV in KC_8. The threshold for interband graphite excitations yields estimates of the Fermi-level shift relative to pristine graphite of 1.4 eV for KC_8 and 1.05 eV for KC_{24}. The spectra of potassium 3*p* excitations suggest that the valence charge density screening the potassium atoms decreases with increasing stage. The spectra of carbon 1*s* core-electron excitations show positive evidence of the hybridization of carbon and potassium wave functions near the Fermi level in KC_8.

Graphite intercalation compounds are novel quasi-two-dimensional materials whose physical properties can be systematically altered by the use of different intercalants or the formation of different "stages." The subsequent changes in electronic structure are central to an understanding of these materials. Among the various intercalants the alkali metals seem to offer the greatest possibility for relatively large perturbations of the graphite electronic structure without the actual formation of strong ionic or covalent bonds which destroy the extended π electron system. This is because metal *s* orbitals are degenerate in energy with the graphite π bands, and the metal atoms are closely spaced in a two-dimensional array occupying the sixfold hollows in the graphite planes. Hybridization between graphite and metal wave functions would be expected, and rather complicated Fermi-surface shapes could result. Of the alkali metals those which form the first-stage compound MC_8 (namely K, Rb, and Cs) have nearest in-plane *M*-*M* distances comparable to the nearest *M*-*M* distances in the corresponding metal and might be expected to exhibit the largest amount of hybridization between metal and graphite bands near the Fermi level.[1] Several detailed calculations of the overall electronic band structure of KC_8 have been carried out which exhibit different degrees of hybridization and Fermi-surface shapes.[1–6] Tests of the overall electronic structure included optical reflectivity measurements[7–9] photoemission measurements,[10,11] and electron-energy-loss studies.[12,13] Because electron-energy-loss measurements yield the momentum-dependent dielectric response function $\epsilon(q,E)$ over a large energy range, they should provide the most detailed tests of the theories from which $\epsilon(q,E)$ can be calculated directly. However, the original energy-loss measurements on potassium-graphite compounds were made with an energy-loss resolution of only 0.7 eV, which is inadequate to accurately measure the shapes of most electronic excitations.[12] In this paper we report high resolution (0.1 eV) electron-energy-loss measurements on several low-stage potassium-graphite intercalation compounds which cover both valence- and core-level excitations with higher signal-to-noise ratios than previous measurements. As a result, more accurate values of the dielectric functions are obtained and fine structures associated with K 3*p* and C 1*s* core excitations can be distinguished.

The samples used in these studies were identical to those used in an earlier work to record the spectrum of back-folded graphite excitations.[14] The sample preparation and handling procedures were described in that paper.[14] The excitations of back-folded graphite bands were observed as several weak but well-defined peaks in the energy-loss spectrum between 20 and 25 eV in KC_8. These features could be explained by a theoretical model involving the excitations of graphite bands which were far removed in energy from the metal *s* states and hence were assumed to be unhybridized. The effect of the metal intercalant was to fold the graphite band structure into a reduced Brillouin zone and to cause splitting and symmetry mixing of conduction-band states as well as symmetry mixing of valence-band wave functions.[14] The spectra reported in this paper focus on excitations closer to the Fermi level where information about hybridization and charge transfer can be obtained.

The raw energy-loss spectra of 80 keV electrons transmitted through thin samples of KC_8 and KC_{24} for a momentum transfer q of 0.1 Å^{-1} parallel to the graphite planes are shown in Fig. 1. Similar to previous measurements[12,13] we measure an intraband plasmon at 2.38 eV and an interband plasmon at 6.23 eV in KC_8. In the stage-2 compound the plasmons are measured at 1.47 eV and 6.67 eV, respectively. In stage 3 they are measured at 1.36 and 6.76 eV. These spectra are qualitatively similar to energy-loss spectra in acceptor-intercalated compounds[15–17] in that the interband plasmon increases in energy with increasing carbon density and the intraband plasmon is relatively much weaker in stage 2 than in stage 1. This latter effect is due to damping of the plasmon at finite q by intervalence excitations which occur in stage-2 materials but not in stage-1 compounds as was described quantitatively for $FeCl_3$ graphite.[16]

The momentum dependence of the intraband plasmons is shown in Fig. 2 where for the sake of clarity the data points have been connected by a smooth curve. These spectra clearly show that the intraband plasmons exhibit the strong positive dispersion which is usually expected for plasma oscillations associated with a free or nearly-free-electron gas.[18] However, dispersion to higher energy only becomes significant at larger values of q where the plasmon is relatively weak due to damping from intraband excitations. The weakness of the plasmons at large q may account for the fact that earlier measurements were unable to detect this dispersion.[12,13]

The momentum dependence of the plasmon energy E_p for a free-electron gas is[18,19]

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

Here m is the free-electron mass, and if v is the velocity, $\alpha = mv^2/2E_{p0}$, where E_{p0} is the plasmon

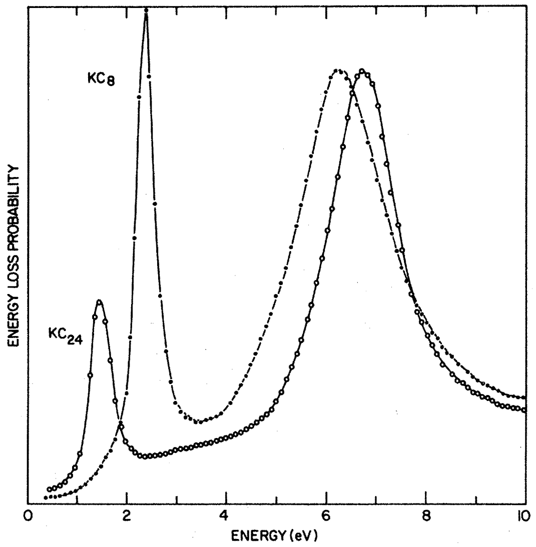

FIG. 1. Energy-loss spectra (points are raw data) in potassium-intercalated graphite compounds for $q = 0.1$ Å^{-1} parallel to the graphite planes.

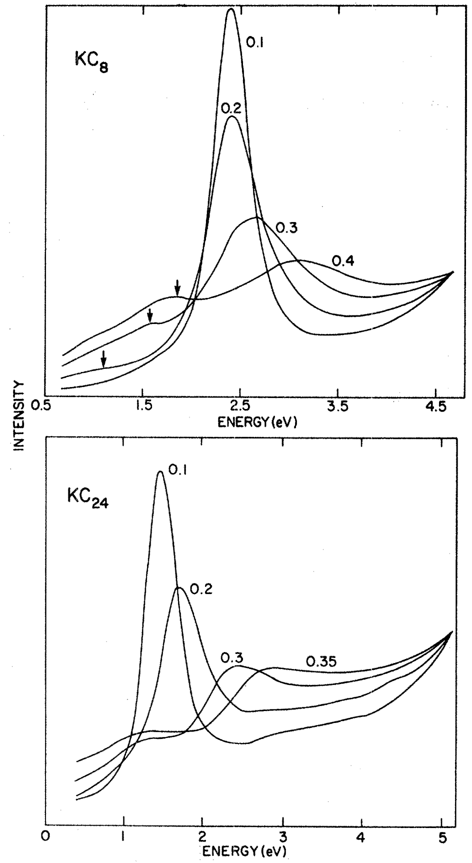

FIG. 2. Momentum dependence of energy-loss spectra for KC_8 and KC_{24} with momentum indicated in Å^{-1}. Arrows indicate peaks in single-particle spectra.

energy at $q=0$. While the charge carriers in intercalated graphite cannot be accurately described by a free-electron gas model,[15,17] the dispersion relation of intraband plasmons in acceptor-intercalated graphite is well fit by Eq. (1). In $FeCl_3$-graphite, $\alpha=1.65$ for stage 1 and $\alpha=2.5$ for stage 2.[16,19] Above $q=0.2$ Å^{-1} the dispersion relations of the intraband plasmons in potassium graphite are also reasonably well described by Eq. (1) with $\alpha=0.8$ for KC_8 and $\alpha=1.74$ for KC_{24}. Below $q=0.2$ Å^{-1} there is no measurable dispersion in KC_8 and less dispersion than expected from Eq. (1) for KC_{24}. The reason for this unanticipated behavior may be that the plasmon dispersion is strongly influenced by the single-particle intraband excitations at large q.

The dispersion of intraband plasmons in KC_8 and KC_{24} is compared with the upper limit for single-particle intraband excitations in Fig. 3. The dashed line is the upper bound for single-particle excitations in two-dimensional graphite sheets in which the electrons obey a dispersion relation $E(k)=\beta|k|$.[15,16] The limit of the single-particle spectrum E_s is then

$$E_s=\beta q \ . \tag{2}$$

This expression is independent of the Fermi level and will be valid as long as the linear dispersion relation is a good approximation to the graphite energy bands. The dashed line in Fig. 3 was then taken from a theoretical model which provided a very good fit to the interband plasmon dispersion in $C_{6.6}FeCl_3$.[15] The upper limit for single-particle excitations in a free three-dimensional electron gas is[20]

$$E_s'=(q^2/2+k_F q)\hbar^2/m \ , \tag{3}$$

where k_F is the Fermi momentum, $k_F=(3\pi^2\rho)^{1/3}$. ρ is the carrier density. In the theoretical model of KC_8 by Inoshita *et al.*[2] there is a roughly spherical region of the Fermi surface centered at Γ composed of metal s states which are partially filled due to incomplete charge transfer. Intraband excitations within these states should follow Eq. (3). If we assume a charge transfer per intercalant atom f of 0.5, we compute an effective k_F of ~ 0.5 Å^{-1}. The resulting intraband continuum described by Eq. (3) is given as the dot-dashed line in Fig. 3. As seen in Fig. 3, plasmons in both KC_8 and KC_{24} run nearly tangent to the intraband continuum for graphite intraband excitations suggesting that these excitations exert the strongest influence on the intraband plasmons. In the random-phase approximation (RPA) theory there is no reason for the plasmon dispersion curve not to intersect the single-particle spectrum. The data in Fig. 3 merely suggest that this does not happen in potassium-graphite compounds over the momentum range we have studied. In addition, our spectra cannot rule out the existence of highly damped three-dimensional plasma oscillations as determined from the analysis of optical reflectivity data.[8] Our analysis merely suggests that at large momenta the dominant contribution to the observed plasmon dispersion comes from two-dimensional graphite excitations.

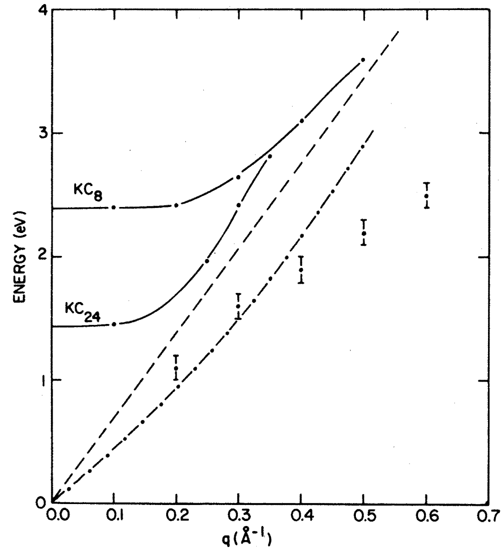

FIG. 3. Intraband plasmon dispersion relation for KC_8 and KC_{24} (solid lines with experimental points shown); upper limit of the single-particle intraband spectra for linear graphite bands (dashed line), and for the model three-dimensional metal bands (dot-dashed line); points with error bars are peaks in the measured single-particle spectra.

Futher evidence indicating the dominance of graphite intraband excitations over any intercalant excitations is given by the observation of the single-particle intraband continuum itself. These excitations are expected to be observable in energy-loss spectra at finite momentum.[20] Peaks in the single-particle continua of KC_8 are indicated by arrows in Fig. 2. Similar but weaker features are measured in KC_{24}. The dispersion of the peaks in the single-particle continua for KC_8 are shown in Fig. 2 as points with error bars. It is difficult to directly compare the peak dispersion with the limits of the single-particle continua given in Fig. 3. Calculations of the spectral shape of the single-particle continua were given for graphite intraband excitations in Ref. 17. There it was shown that at small q (~ 0.1 Å^{-1}) the peak in the continuum is quite near the upper limit, but at large q (>0.2 Å^{-1}) the peak falls considerably below the upper limit of the single-particle spectrum. Thus, the strongest contributions to the single-particle spectra cannot be intraband excitations in partially filled metal s bands, since the measured peaks are above or very near the dot-dashed line which defines the upper limit of the expected continuum as shown in Fig. 3. On the other hand, the peak dispersion is quite reasonable for graphite intraband excitations.

The spectra of intra- and interband excitations in KC_8 and KC_{24} at $q=0.1$ Å^{-1} for energies up to 20 eV are given in Fig. 4, where the real and imaginary parts of the dielectric function are plotted. These functions were obtained from the energy-loss spectra which were measured up to 40 eV. The spectra were corrected for multiple inelastic scattering and normalized so as to yield $\mathrm{Re}(1/\epsilon)=0$ at $E=0$ using well-established methods.[17] The present samples were quite thin and only a small multiple-scattering correction was necessary. While the value $\mathrm{Re}(1/\epsilon)=0$ at $E=0$ is only correct at $q=0$, the relatively small dispersion of the intraband plasmons at small q justifies the use of the $q=0$ value.

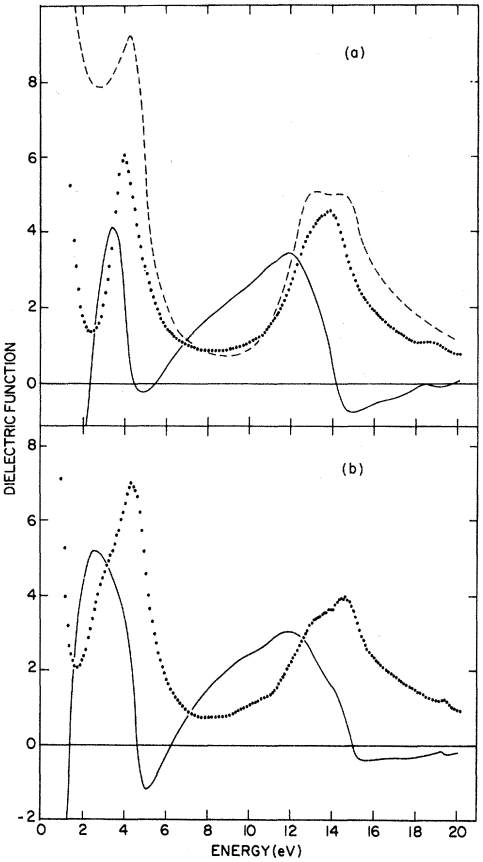

FIG. 4. Dielectric functions for (a) KC_8 and (b) KC_{24} at $q=0.1$ Å^{-1}. ϵ_1 is shown as a solid line, ϵ_2 is the actual data points and is shown for pristine graphite as a dashed line.

In Fig. 4 we note that ϵ_2 is very large at low energy due to intraband excitations which decrease rapidly with increasing energy. However, at 2.5 eV in KC_8 and 1.8 eV in KC_{24} there is a turning point in ϵ_2 due to the increasing strength of interband excitations which are predominantly in the graphite planes. From Fig. 4 we can estimate the onset of the interband threshold at $q=0.1$ Å^{-1} using the graphical methods applied to $C_{6.6}FeCl_3$.[17] We then correct for the dispersion of the graphite energy bands with momentum so as to obtain an estimate of the interband threshold at $q=0$. This threshold is estimated to be 2.8 ± 0.2 eV in KC_8 and 2.1 ± 0.2 eV in KC_{24}. The interband threshold is essentially double the amount by which the graphite Fermi level has been raised. Hence, we estimate that the Fermi level is raised 1.4 eV in KC_8 and 1.05 eV in KC_{24} relative to that in pristine graphite. For KC_8 this value is identical to what was reported in photoemission experiments[10,11] and is good agreement with theoretical values of 1.3 eV by Inoshita *et al.*[2] and 1.43 eV by DiVincenzo *et al.*[6]

From the value of the shift in the Fermi level, the amount of charge transfer can in principle be determined.[21] Using the linear density of states appropriate for acceptor-intercalated compounds,[21] we calculate that the charge transfer per carbon atom is 0.06 electrons in KC_8 and 0.034 electrons in KC_{24} resulting in $f=0.5$ and 0.8 in KC_8 and KC_{24}, respectively. While these numbers are in reasonable agreement with some theoretical estimates,[2] a Fermi level shift of 1.43 eV in KC_8 is accompanied by complete charge transfer ($f=1$) in other models.[6] Clearly the results depend critically on the model for the density of states which is used. Unfortunately, it is the Fermi-level position rather than the charge transfer which can be directly measured by several methods. More importantly, the definition of f in donor-intercalated compounds may be rather nebulous. If metal and potassium wave functions are hybridized, then a simple method for defining "charge transfer" is not possible. In LiC_6 a completely empty metal-like band would seem to indicate that $f=1$, but calculations of the valence charge density in the region around the Li site show a charge distribution similar to the Li 2*s* orbital with the actual charge density at the Li site being quite comparable to that in a Li atom.[1] Similar effects may occur in KC_8.[6] Thus, although one can produce a number for the charge transfer based on a measurement of the Fermi level this result may be of limited utility.

Above the threshold of the interband excitations, ϵ_2 of KC_8 shows a smooth sharp peak at 4.0 eV with a width of about 1.4 eV. As shown in Fig. 4 this structure differs considerably from ϵ_2 for pristine graphite which has a peak at 4.3 eV and much stronger interband absorption than in KC_8 over the entire spectral range. Below 20 eV, ϵ_2 in KC_8 is generally lower than ϵ_2 in graphite because the potassium contributes only 1 electron which can be excited in this energy range, while the unit-cell volume increases by 60%. The number of oscillators per unit volume which can be excited is lower in KC_8 than in graphite. Using the data in Fig. 4(a) we can calculate the integral from 0 to 20 eV of ϵ_2 times the energy for KC_8 and graphite as a measure of the relative oscillator strengths. The ratio of these integrals (KC_8:graphite) is 0.70 while the ratio of the *c* axis distances (graphite:KC_8) is 0.62. If one takes into account the extra electron contributed by the potassium there is quite reasonable quantitative agreement between the relative oscillator strengths and the volume ratio.

In KC_{24}, ϵ_2 more closely resembles that of pristine graphite with a peak at 4.3 eV and a shoulder at 3 eV reminiscent of graphite interband absorption which has been cutoff by the raised Fermi level. A qualitatively similar dielectric function was measured in stage-2 $SbCl_5$ graphite where the lowered Fermi level also creates a gap in the interband absorption spectrum.[22] The qualitative features of these dielectric functions are in reasonable agreement with the earlier measurements which had poorer resolution.[12,13] The present results are also more consistent with the predictions of DiVincenzo *et al.* than with other band-structure calculations.[12,13] The most recent KKR (Korringa-Kohn-Rostoker) results indicate that the *M*-point interband transition in graphite (which we measure at 4.3 eV) is down shifted and split into a series of interband transitions centered at 4.1 eV.[6] These transitions span a region of 1.4 eV and could account for the width of the peak in ϵ_2 which we observe. On the other hand, we do not resolve any structure in this region which might be identified with specific individual interband excitations. Moreover, until the oscillator strength for each of the series of interband transitions is calculated, a quantitative comparison between theory and experiment cannot be made.

Above the *M*-point interband transitions, a strong peak between 13 and 15 eV associated with σ band excitations is observed in pristine graphite which is also present in the intercalation compounds.[17] In the potassium-graphite compounds the structure in this peak is somewhat different than in pristine graphite. Since hybridization between metal orbitals and graphite σ bands is not likely,[1] the differences in the structure near 14 eV cannot be easily explained at this time. At yet higher energy we observe in Fig. 4 the onset of absorption due to the potassium intercalant in the region between 18 and 20 eV.

The best method for checking the results of a Kramers-Kronig analysis of electron-energy-loss data is to compute the optical properties from the resulting dielectric function and to compare the results with accurate optical measurements. This comparison is carried out for KC_8 in Fig. 5 using the published optical data of Zanini and Fischer.[8] The optical spectra were recorded on a sputter-etched *a* face and hence may not accurately give the absolute reflectivity due to scattering from surface defects. New measurements of the absolute spectral dependence of the reflectivity from a *c* face are shown as the open circles in Fig. 5.[23] These data agree very well with the reflectivity of KC_8 calculated from the dielectric function of Fig. 4. The absolute magnitude of the reflectivity at

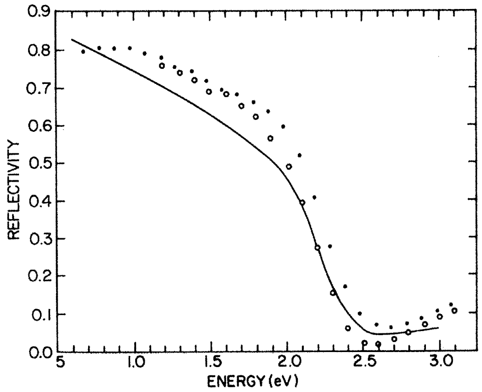

FIG. 5. Optical reflectivity computed from energy-loss data (closed circles), compared with measured *a*-face spectrum (Ref. 8) (solid line) and *c*-face spectrum (Ref. 23) (open circles).

low energy and the position of the plasma minimum near 2.5 eV are well accounted for. The reflectivity computed from the energy-loss spectra appears to be systematically shifted by ~ 0.1 eV to higher energy as compared with optical measurements. Since the intraband plasmon is dispersionless at low q, the reason for this shift is not obvious. While reflectivity data specific to KC_{24} have not been published, we have compared our computed reflectivity for this compound with that reported by Guerard *et al.*[7] for RbC_{24} since there are no reports of significant differences in the low-energy optical properties of the heavy alkali metal intercalation compounds. The energy-loss data predict a plasma edge with a minimum in reflectivity at 1.7 eV in good agreement with the optical results.[7] However, since the spectra were measured at finite q where the plasmon in the stage-2 material is strongly damped, the maximum in the predicted reflectivity at 0.6 eV was calculated to be only 67% vs 86% measured. This type of discrepancy is unavoidable since optical data correspond to $q = 0$ and in cases like KC_{24} where relatively large spectral changes occur for small values of q, precise agreement with measured optical properties is impossible.

At higher energy the reflectivity spectra calculated from electron-energy-loss spectra for KC_8 and KC_{24} resemble the measured optical spectra for cesium compounds.[11] In KC_{24} a relatively sharp peak in reflectivity is computed at 5.0 eV with a maximum reflectivity of 36%. In KC_8 the calculated reflectivity spectrum shows a broader and weaker peak centered at 4.5 eV with a maximum reflectivity of 29%. As pointed out in the optical studies[11] the differences between the optical properties of KC_8 and KC_{24} indicate that the electronic structure of KC_8 is significantly different from pristine graphite, whereas the KC_{24} spectra are much more graphitelike. These differences are embodied in the dielectric functions shown in Fig. 4.

As illustrated in Fig. 6, the energy-loss spectra of potassium-graphite intercalation compounds also contain sharp features associated with the absorption threshold of the potassium $3p$ electrons. Sharp but weak peaks are measured at 18.42 eV in KC_8, 19.17 eV in KC_{24}, and 19.32 eV in KC_{36}. These excitations are from the K $3p$ core state to the bottom of the K $4s$ conduction band, and clearly show the trend of increasing transition energy with increasing stage. Core-level excitation energies depend on the binding energy of the initial state, the final-state energy, and the screening of the excitation by the electronic charge density both on the particular atomic state and on neighboring atoms. A measurement of the transition energy alone cannot determine the relative significance of these effects. A measurement of the binding energies of the K $3p$ core states by photoemission spectroscopy would help to establish whether the stage dependence of the core excitations was due to binding-energy differences alone. In the absence of such measurements we can only speculate as to the origin of the observed trend. In the first stage Li compound LiC_6 deeply bound carbon π electrons hybridize with the Li $2s$ states to strongly screen the Li site while the bulk of the Li $2s$ states form an empty free-electron-like band above the Fermi level.[1] Recent calculations indicate that similar effects occur in KC_8.[6] The valence charge density at the metal site will lower the core-level excitation energy by decreasing the binding energy of the initial state and screening the excitation. The fact that the K $3p$ excitation occurs at higher energy in higher-stage compounds may be due to less π electron density at the metal site in these materials. The deeply bound carbon π electrons could take on less metal-like character in the higher-stage materials since there are fewer metal atoms with which to interact. However, this question will only be resolved when detailed calculations of filled and empty states and their charge distribution are made for potassium compounds as a function of stage.

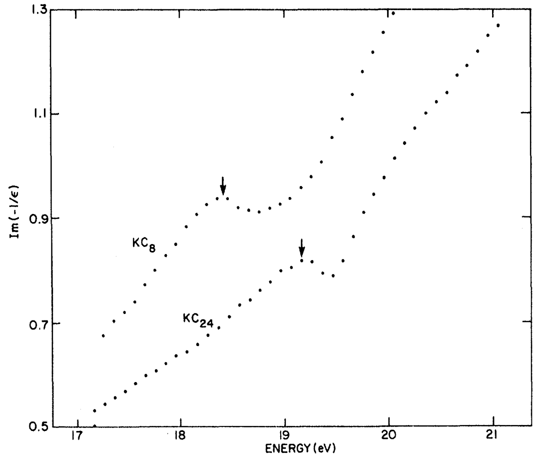

FIG. 6. Potassium $3p$ excitations as measured in energy-loss spectra of KC_8 and KC_{24}.

The excitations near the absorption edge of the carbon $1s$ core electrons in potassium-graphite compounds are shown in Fig. 7. Each panel shows

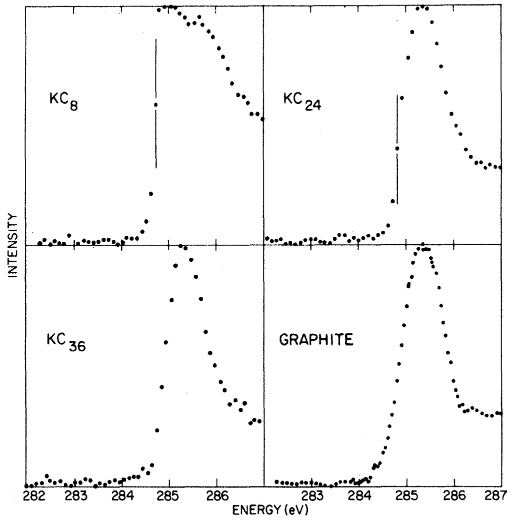

FIG. 7. Carbon 1*s* excitation spectra (raw data). Vertical lines indicate Fermi-level cutoff.

the excitation spectra of 1*s* electrons into the empty states just above the Fermi level in the different materials. In KC_8, transitions to the Fermi level are characterized by the extremely steep rise indicated by a vertical line. There are two peaks separated by 0.7 eV above the Fermi-level cutoff. The overall spectrum is considerably broader than is observed in pristine graphite. KC_{24} shows less of a discontinuity at the Fermi level and a spectrum more like that of graphite, while KC_{36} exhibits an absorption line shape nearly identical to graphite although some minor shape differences persist. The spectra in Fig. 7 stand in marked contrast to similar spectra in acceptor-intercalated compounds.[21,22,24] In these materials the Fermi level is simply lowered, and above the pristine graphite Fermi level the spectrum of transitions to conduction-band states is identical to that in pristine graphite.[21,22,24] Thus, in acceptor-intercalated compounds the states just above the Fermi level are not perturbed by the intercalant. This is clearly not the case in KC_8. A double-peaked spectrum could be explained by hybridization between carbon and metal wave functions in such a way that excitations from the carbon 1*s* core level take place to states with amplitude on the carbon site which were derived from metal as well as carbon orbitals. The semiempirical tight-binding model of Inoshita *et al.*[2] for KC_8 shows a density of states above the Fermi level characterized by a peak at the Fermi level due to metal-like orbitals followed by a peak 0.5 eV higher which contains states closely related to states at the *M* point of pristine graphite. While this model seems to describe the measured spectra reasonably well it is not possible to directly compare the carbon 1*s* spectrum with the ground state density of states. This is because the electron-hole interaction strongly influences the spectral shape resulting in excitonic enhancement of the absorption edge.[24] In the analysis of core exciton spectra of acceptor-intercalation compounds, the electron-hole interaction was taken into account and an excellent fit to the measured line shape obtained.[24] However, due to the obvious similarities with pristine graphite spectra only carbon π orbitals were used in this analysis.[24] To properly analyze the line shape of core-excitons in KC_8, hybridized carbon and metal bands must be used. When this is done the present spectra may be able to distinguish between the various theoretical models of KC_8.[2–6]

An alternative explanation for the double-peaked structure observed for KC_8 would be that there are different carbon 1*s* binding energies associated with the two inequivalent carbon sites in this material and that this results in two separate absorption edges. In KC_8 each carbon atom can have either one or two potassium nearest neighbors. This type of argument has been advanced to explain the anomalously large width (~ 2.2 eV) observed in x-ray photoemission spectra of KC_{24}.[25] However, these types of effects cannot have much relevance to the spectra reported here. The spectral peak we measure in KC_{24} is only slightly broader than that of pristine graphite (~ 1.1 eV wide). There is no evidence for chemical shifts of ~ 2 eV. The splitting of 0.7 eV in KC_8 would be difficult to resolve with standard ESCA (electron spectroscopy for chemical analysis) spectrometers. Nevertheless, if the double peak we observe in KC_8 were due to two inequivalent carbon sites then we would expect to measure two absorption edges with relative intensity given by the relative numbers of the different sites, namely 1:1. The spectrum of KC_8 in Fig. 7 is incompatible with this requirement. The second peak is very much weaker than the peak at the absorption edge and the inequivalent site hypothesis suggests that it should be just as strong. Hence, the ususual line shape of the C 1*s* spectrum of KC_8 shown in Fig. 7 is not due to inequivalent carbon atoms. It can only be due to a distribution of carbon conduction-band states influenced by hybridization with metal wave functions.

In this paper we have described the measurements of valence- and core-level excitations in potassium-graphite intercalation compounds. Carbon 1s core-level spectra show that carbon and metal wave functions near the Fermi level in KC_8 are hybridized. Valence excitations, as characterized by the dielectric function, show that interband transitions in KC_8 differ significantly from pristine graphite while in higher stages these transitions are more graphitelike. From the onset of the interband transitions a measure of the Fermi level was obtained, and from this measurement an estimate of the charge transfer was given using a particular model density of states. Potassium 3p core-level spectra suggest that the valence charge density screening the potassium atoms decreases with increasing stage. At the lowest energies studied, the momentum dependence of intraband excitations was shown to be dominated by graphite excitations, and intraband plasmons (influenced by the single-particle intraband spectrum) were shown to have strong positive dispersion.

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