Electronic Structure of Alkali-Intercalated Graphite Studied by Soft—X-Ray Emission Spectroscopy

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Carbon K soft–x-ray emission spectra of LiC_6, KC_8, and CsC_8 are presented. An absolute value for the charge transfer from the alkali metal to the carbon π band is obtained. A model fit to the data reveals similar effects on both spectral shape and threshold energy, independent of the choice of the alkali-metal intercalant, and provides a measure of departures from the rigid-band approximation. An enhancement of the soft–x-ray emission spectrum near E_F is reported.

It is commonly accepted through many theoretical and experimental studies that in alkali-metal–graphite intercalation compounds (AGIC's), donor electrons from the alkali atoms are introduced into the previously empty carbon π^* antibonding conduction band, raising the Fermi level and increasing the density of states at the Fermi level relative to that of graphite.[1] However, existing electronic structure calculations conflict on the position of the metal band relative to the Fermi energy, consequently on the amount of charge transfer of the metal valence electrons to the graphite π^* band, and on the character of the first unoccupied band.

Both theoretical[2] and experimental[3] studies agree upon Li 2s states in LiC_6 being well above the Fermi energy, implying a nearly complete charge transfer from lithium to carbon. The case of heavier AGIC's MC_8 (M = K, Rb, and Cs), on the other hand, is far from being resolved. Some experiments on KC_8,[4] K layers on graphite,[5] Cs layers on graphite,[5b,6] and theoretical studies[7] support a description in which the metal state lies above E_F and is unoccupied, while on the other hand a number of experiments[8] favor the incomplete–charge-transfer picture, in agreement with earlier band-structure calculations.[9] Most of the above experiments provide an indirect measure of the charge transfer. The only one to directly measure this quantity is the x-ray photoemission spectroscopy result of Preil and Fischer[4] which is consistent with complete charge transfer for KC_8. The only concern about that determination is its surface sensitivity.

It might seem that Knight-shift measurements can provide a direct measure of the charge transfer. The Knight shift allows a determination of $|\psi(0)|^2$, the charge density of conduction electrons at the nucleus. This quantity does not change greatly, however, when the outermost alkali electron is transferred to the π

band.[8b] The π wave function overlaps the alkali-metal-atom nucleus and the substantial nuclear Coulomb potential maintains $|\psi(0)|^2$ at a large value.

Very recently, Takahaski and co-workers,[10] using angle-resolved ultraviolet photoemission spectroscopy, stirred up the controversy even more by reporting a charge transfer of about 0.5 unit electronic charge for both KC_8 and CsC_8 from a quantitative estimate of the electron population in the observed dispersive π^* band. However, in addition they observe a nondispersive partially filled band just below the Fermi energy, whose properties do not correspond to any theoretical model and whose occupation they could not estimate.

In this Letter, we report a soft–x-ray emission spectroscopy (SXE) study of the carbon K spectra of LiC_6, KC_8, and CsC_8. A preliminary version of these results was presented at the Vacuum Ultraviolet Eighth International Conference in Lund.[11] Eisberg *et al.* also described SXE measurements of KC_8 at that meeting which are consistent with the results we present here.[12]

The spectrograph used in this work has been previously described.[13] Briefly, the sample is excited by a 3-kV electron beam (beam size = 0.1 × 1 mm², beam current = 0.1 mA), and the emitted x rays dispersed by a grazing incidence toroidal holographic diffraction grating and detected by a phosphor-coated photodiode array. The samples were transferred from sealed glass ampoules to a vacuum airlock through pure nitrogen atmosphere, cleaved *in situ* at 10^{-6} Torr and quickly moved into the spectrometer where the pressure is approximately 10^{-9} Torr. Typically, a freshly prepared surface remains clean looking (i.e., golden as opposed to blue or black) for approximately half a day under these circumstances. The carbon K emission spectra reported here were obtained in short runs of 10 to 30 min to avoid beam damage. Using the Feldman[14] empirical range

formula, we estimate the electron beam used for excitation to penetrate approximately 2000 Å (LiC_6), 1200 Å (KC_8), and 800 Å (CsC_8) into the sample so any serious distortion from surface contamination (or surface states) is avoided. The calibration accuracy in the energy range of interest and the instrumental resolution are 0.2 eV.

Emission from highly oriented pyrolytic graphite (HOPG) and AGIC's is anisotropic, with σ and π valence electrons contributing differently to the emission spectrum at any given angle. By varying the take-off angle of the x-ray emission relative to the sample normal, these contributions can be separated.[15] We subtract our estimate of the radiative Auger contribution from the data in order to get the one-electron transition density of states (TDOS).[16] Since only one π electron is available to contribute to the emission, the HOPG π band is normalized such that its area is one electron. The AGIC π bands are then scaled in overall amplitude to best match that of HOPG in the lower region (265–282 eV). Figure 1 shows the HOPG π band plotted on top of that of LiC_6, KC_8, and CsC_8, and shifted down in energy by 0.66, 0.92, and 0.65 eV, respectively. This energy shift is peculiar to the lower π band since the core level and the σ band moved together upon intercalation in the three compounds. While no significant changes in the shape of

FIG. 1. π bands obtained from carbon K emission spectra for AGIC's (dots) and HOPG (line), with HOPG shifted down in energy by 0.66, 0.92, and 0.65 eV, for LiC_6, KC_8, and CsC_8, respectively.

the AGIC σ bands relative to that of graphite have occurred as a result of the alkali-metal intercalation, the corresponding π bands resemble that of HOPG, but with an added contribution at the top of the band. The presence of this sharp peak is the most direct evidence of charge transfer from the alkali into the carbon π^* antibonding electron conduction band. Qualitatively this is just what is expected from the point of view of the rigid-band model: Donor electrons from the alkali-metal atoms have filled some of the empty carbon π states, raising the Fermi level and correspondingly increasing the density of states at the Fermi energy. The normalized spectra represent now the TDOS expressed in states/eV carbon-atom, allowing us to determine the area under LiC_6, KC_8, and CsC_8 π bands with the results: 1.26, 1.20, and 1.20, implying a charge transfer of 0.26, 0.20, and 0.20 electrons per carbon atom, respectively.

Since complete charge transfer, corresponding to 0.167 electrons per carbon atom, is expected in the case of LiC_6, our experimental determination implies an enhancement of the TDOS near the Fermi energy by a factor of 0.26/0.167 = 1.56. This enhancement is due to changes in the carbon π wave functions caused by the annihilation of the core hole as described below. We expect those wave functions to be quite similar for different alkali-metal intercalants, therefore giving rise to approximately the same enhancement of the TDOS. Applying the same factor for KC_8 and CsC_8 as LiC_6, we find a charge transfer of 0.128 and 0.128, respectively, in agreement with complete charge transfer for these compounds as well, and consistent with Preil and Fischer for KC_8.[4]

Such an enhancement of the intensity near the Fermi energy has been observed in AGIC Auger spectra by Murday et al.[17] When deconvoluted, their Auger measurements indicated a TDOS enhancement of a factor of 4. They predicted the same enhancement to occur in SXE, and attributed it to screening of the initial core hole by the conduction π electrons. To explain such a result, Dunlap, Ramaker, and Murday[18] extended the orthogonalized–final-state-orbitals approximation of Davis and Feldkamp[19] to Auger decay, and showed that it qualitatively, if not quantitatively, accounted for the observed enhancement.

We normalized the local density of states presented in Ref. 17 such that the integral of the original graphite π band corresponds to 1.0 electron. With the assumption of complete charge transfer for LiC_6, the calculated enhancement is then given by the ratio of the normalized value of the local density of states at E_F to 0.167. However, because of the coarse energy spacing used in the published calculation, we are unable to precisely determine the enhancement, and can only estimate an upper and lower limit of 2.1 and 1.2, respectively. These values are to be compared with our experimental result of 1.56, and to the factor of 4 obtained in the Auger-electron-spectroscopy experiment. The discrepancy in the ampli-
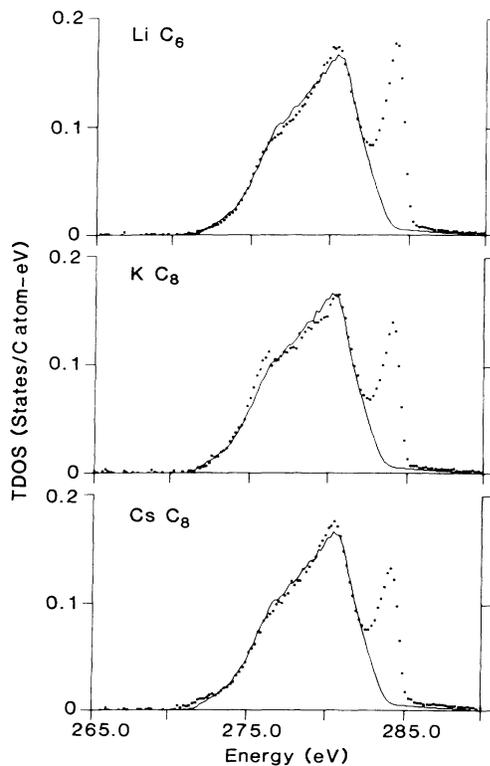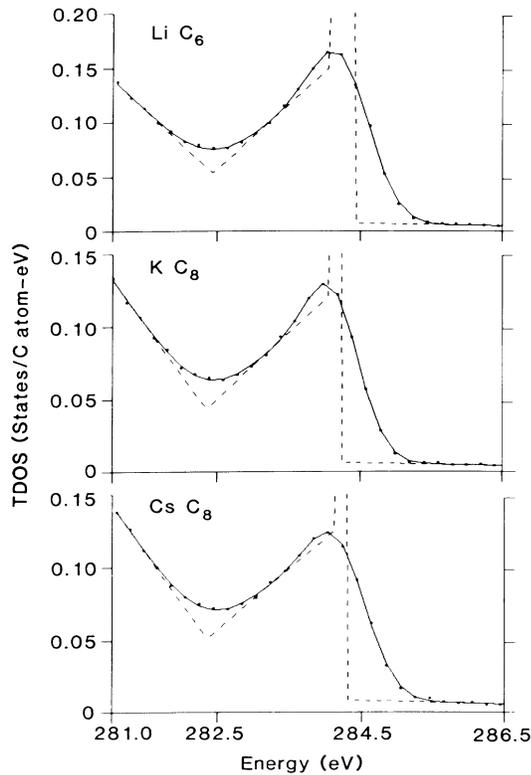
FIG. 2. Step-function model fit to upper part of AGIC's π subband, with the dots, full line, and dashed line representing the data points, the fit to the data, and the unbroadened model, respectively.

tude of the enhancement as seen by SXE and Auger-electron spectroscopy is quite unexpected, as Dunlap, Ramaker, and Murday,[18] along with Murday et al.,[17] predicted the same enhancement to occur in the two processes. The orthogonalized–final-state-orbitals approximation[19] is quantitatively in better agreement with the SXE than the Auger-electron spectroscopy measure-

ment. Two fundamental physical differences between the two techniques, namely, different transition-matrix elements, and the fact that the final state in the Auger process has two valence holes versus one in the x-ray case, may account for such discrepancy. Clearly, such an enhancement still awaits more theoretical and experimental implementation in order to explain both its occurrence and amplitude.

Thus we find that the core hole influences the shape of the emission spectrum in violation of the "final-state rule," which is known to work well for simple metals.[20] This rule asserts that the transition density should be calculated from wave functions obtained in the potential of the final state of the x-ray process and therefore the core hole should be ignored.

Another approach to understanding our data is to fit them with a model. According to band-structure calculations,[21] the density of states near the top of the valence band of graphite descends nearly at zero at the Fermi energy. The density of unfilled states in the conduction band then rises linearly. Following recent band-structure calculations,[7a,9a,22] we modified such a model by adding a step function of adjustable width W, and whose height is determined by the value of the density of states at the Fermi energy, $D(E_F)$, as derived from specific-heat measurements.[23] The step, resulting from the enhancement of the density of states at the Fermi level upon intercalation, is a common feature of all the above calculations and has been ascribed to the hybridization of carbon and alkali-metal bands.[9a] Accounting for disorder and phonon broadenings, we then convoluted that shape with a Gaussian broadening function to fit the data. Figure 2 shows the fit and the unbroadened model for comparison. Table I shows the parameter values. We calibrate the vertical scale for determining the absolute value of the area under the alkali-metal-filled π states by subtracting from the total π band the area the alkali contributes as given by the model, and then scaling this value to unity. The results are 0.29, 0.21, and 0.22

TABLE I. Model parameters for AGIC's. The numbers in parenthesis have been corrected for the excitonic enhancement as described in the text. E_F, Fermi energy as seen in emission; ΔE_F, shift in Fermi energy upon intercalation; W, width of step function at Fermi energy; σ_v, standard deviation of Gaussian broadening of valence band; σ_c, standard deviation of Gaussian broadening of conduction band; S_v, slope of valence band; S_c, slope of conduction band; A, amplitude of TDOS at its minimum value just below E_F; and $D(E_F)$, amplitude of TDOS at E_F.

	E_F (eV)	ΔE_F (eV)	W (eV)	σ_v (eV)	σ_c (eV)	S_v $\left[\dfrac{\text{states}}{(\text{C atom})\,\text{eV}^2}\right]$	S_c	A $\left[\dfrac{\text{states}}{(\text{C atom})\,\text{eV}}\right]$	$D(E_F)$[a] $\left[\dfrac{\text{states}}{(\text{C atom})\,\text{eV}}\right]$
LiC_6	284.4	1.98	0.32	0.46	0.39	0.059 (0.038)	0.061 (0.039)	0.044 (0.028)	0.33 (0.21)
KC_8	284.2	1.86	0.12	0.45	0.36	0.065 (0.042)	0.047 (0.030)	0.035 (0.022)	0.55 (0.35)
CsC_8	284.3	1.96	0.19	0.47	0.39	0.067 (0.043)	0.043 (0.028)	0.041 (0.026)	0.34 (0.22)

[a]From specific heat; see Ref. 21.

electrons/carbon atom for LiC_6, KC_8, and CsC_8, respectively, in excellent agreement with the above determination. The differences between these numbers and those obtained above give us an estimate of the overall uncertainty in our evaluation of the enhancement factor and the charge transfer. We estimate these uncertainties to be 10% of the corresponding value.

As an additional confirmation of the similarity of the spectral shapes for the alkali-metal intercalants Li, K, and Cs, the Fermi-energy shifts ΔE_F, and the standard deviations of the Gaussian broadening of the valence and conduction bands, σ_v and σ_c, are independent of the choice of the intercalant. A similar conclusion was drawn by Grunes and Ritsko[24] using electron-energy-loss spectroscopy. We can also compare our measured values corrected for the enhancement (see Table I) of the slopes of the valence and conduction bands, S_v and S_c, and A, the amplitude of the TDOS at its minimum value just below E_F with calculations. Our measurements of both of these parameters are consistent with calculations for HOPG.[21,25,26] For the AGIC's some theoretical values are Holzwarth, Rabii, and Girifalco[22] for LiC_6 ($S_v = 0.081$, $S_c = 0.073$, and $A = 0.015$); Inoshita, Nakao, and Kamimura[9a] for KC_8 ($S_c = 0.111$, and $A \approx 0$); and DiVincenzo and Rabii[7a] for KC_8 ($S_v = 0.087$, $S_c = 0.071$, and $A \approx 0$). The major discrepancy with our measurements is that our value for A is larger than predicted.

In conclusion, we have shown how SXE spectra of AGIC's represent direct evidence of charge transfer from the alkali metal to the carbon π bands, how such charge transfer can quantitatively be estimated, and how the SXE spectra are enhanced, in qualitative agreement with Auger measurement.

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