Evidence for an Alkalilike Conduction Band in Alkali Graphite Intercalation Compounds

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The valence bands of pure graphite and several alkali graphite intercalation compounds were studied by ultraviolet photoelectron spectroscopy ($h\nu = 21.2$ eV). The most significant observation is an intensity peak at the Fermi energy E_F in the intercalation compounds. This peak is mainly due to alkalilike s states. The density of states at E_F is enhanced by a factor of 30 compared with pure graphite. The alkalilike conduction bands in the first stage alkali graphite interclation compounds are similar to those of pure alkali metals.

Graphite intercalation compounds (GIC's) are presently the object of many investigations.[1] Their high electrical conductivity, their optical properties, and other features could make them useful for several applications. As the electronic properties of these materials are far from being clearly understood, several attempts have recently been made to investigate their electronic structure.[2-9] Of central importance is the electronic band structure which is responsible for the metallic behavior. In particular, the changes of the band structure, the Fermi energy E_F, and the density of states (DOS) at E_F on intercalating pristine graphite are of interest. In this work, we report the first photoemission studies of a series of alkali graphite intercalation compounds (AGIC's).

Stage-1 compounds C_8K, C_8Rb, C_8Cs and higher-stage cesium compounds $C_{12n}Cs$ ($2 \geqslant n \geqslant 7$) were prepared by the two-temperature method in Pyrex vessels.[10] Slabs of the highly oriented pyrolytic graphite (HOPG) (obtained from Union Carbide) were used. The dimensions of the specimens were typically of the order $0.6\times1\times0.1$ cm^3. The stage and homogeneity of the samples were checked by x-ray diffraction both before and after the measurements. The samples were transferred under argon into the preparation chamber of a combined x-ray photoemission spectroscopy (XPS)/ultraviolet photoelectron spectroscopy (UPS)/ Auger electron spectroscopy (AES) spectrometer (Leybold-Heraeus) and cleaved *in situ* after reaching ultrahigh vacuum. After cleaving of the samples no contaminants could be detected by XPS (Mg $K\alpha$ excitation) or AES. The base pressure in the measuring chamber was in the 10^{-11}-Torr range and in the lower 10^{-9}-Torr range during the UPS measurements. The composition of the samples within the electron escape depth was checked by XPS core-level intensity comparison. No deviation from the bulk composition given by stage number and stoichiometry could be detected even for high stages. We conclude that the surface composition is well averaged over the microcrystallites from which a cleaved macroscopic GIC surface is built up. The resolution of the UPS measurements was 0.1 eV. The angle of the incident photons was at 60° to the surface normal and the detected photoelectrons were emitted in a cone of 30° perpendicular to the surface of the samples which was parallel to the graphite layers. All UPS spectra are plotted without any corrections of background subtraction.

Figure 1 shows the UPS ($h\nu = 21.22$ eV) valence-band (VB) spectra of pristine graphite and the AGIC C_8Cs. Our UPS spectra for pure graphite are in good agreement with published XPS spectra[11] by taking into account the different cross sections of the $2s/2p$ states in both experiments. Our measurements revealed four distinctive structures at binding energies of 3.0, 4.7, 8.0, and 12.3 (± 0.1) eV respectively, which can be attributed to flat π bands near the symmetry point Q and flat σ bands near the symmetry points Γ, Q, and P, respectively, in the energy-band structure of graphite.[11,12] The structures at 3.0 and 4.7 eV are marked by A and B as shown in Fig. 1. Apart from the E_F region, the spectra of pure graphite and the AGIC are very similar: The four structures are weakened but can still be observed. In the vicinity of E_F, the spectra of both materials *differ significantly*: The most striking feature is the occurrence of a pronounced intensity peak at E_F in the AGIC synthetic metal, whereas the intensity of the HOPG semimetal spectrum is very small. In the discussion, we will provide strong evidences that this peak is caused by alkalilike states. All the AGIC spectra were plotted in such a way that the structures A and B are at the same binding energies and that the intensities at 4.7 eV have the same value as in pure graphite.

In Fig. 2 the VB's of the three donor compounds

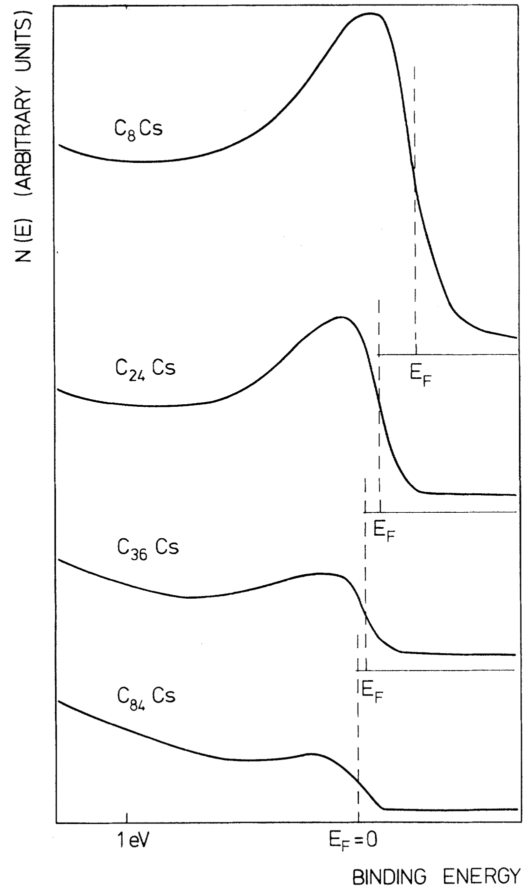

FIG. 1. UPS spectra of C HOPG and C_8Cs ($h\nu = 21.2$ eV). The energy scale of the GIC spectrum is shifted in such a way that the graphite features *A* and *B* are at the same position. The spectra are normalized to the same intensity at the peak *B*.

C_8Cs, C_8K, and C_8Rb are compared. The curves are all very similar. The intensities of the maxima at E_F for C_8K and C_8Rb are somewhat reduced compared with C_8Cs. The shift of E_F increases on going from Cs to K and to Rb and is given by 1.0, 1.4, and 1.8 eV, respectively.

In Fig. 3 the spectra of different stages of Cs GIC's close to E_F are shown in an expanded energy scale. The intensity of the VB's of the alkali metal decreases with increasing stage; *by contrast*, the changes in the Fermi level shift with increasing stage are very small: 1 eV for stage 1 and still 0.7 eV for stage 7. In addition, the VB peak at E_F in C_8Rb was studied by low-energy photoemission ($h\nu \leq 6.5$ eV).[13] The bandwidth and the shape are very similar to the UPS ($h\nu = 21.2$ eV) results. Therefore, we conclude that the peak at E_F is not due to structures in the final states but rather reflects the density of the occupied states.

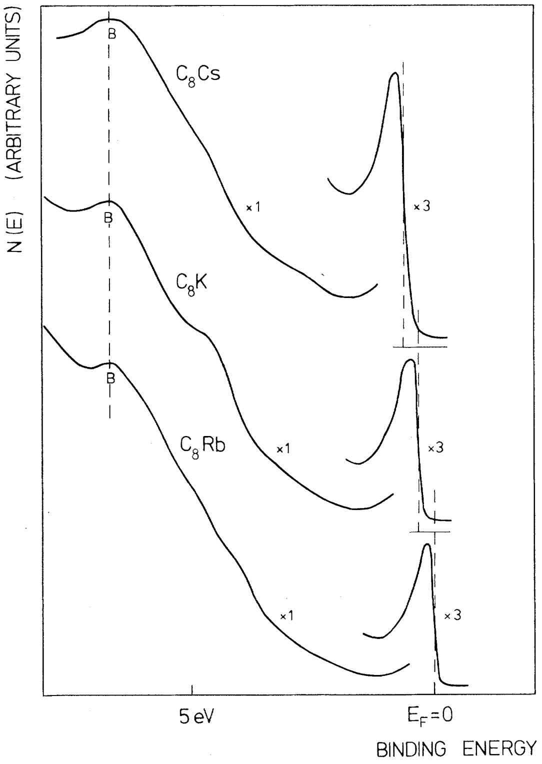

FIG. 2. UPS spectra for C_8Cs, C_8K, and C_8Rb ($h\nu = 21.2$ eV). Normalization of the intensity and shift of energy scale as in Fig. 1.

In the following, we discuss what information can be gained concerning the DOS at E_F, the shift of E_F in the various compounds, the shape and bandwidth of the VB, and the encountered charge transfer.

The observed dependence of the DOS at E_F *as a function of the alkali-metal concentration* in Cs GIC's shows unambiguously that the DOS peak at E_F is mainly due to the *s* electrons of the intercalated alkali metal (Fig. 3). The measured values for the DOS with increasing E_F from 0.7 to 1 eV within the Cs compounds cannot be fitted in any way with the graphite π-conduction-band DOS given in Ref. 5.

The Auger *KVV* spectra of HOPG, C_8Cs, and C_8Rb (Ref. 9) give clear evidence that one introduces *additional* states of a new type on top of the graphite VB's by intercalation of alkali metals. These states do not affect the graphite *KVV* spectrum, therefore are self-convoluted and not of the carbon *p* type nor of the carbon *s* type. The shape and bandwidth of the features at E_F are very similar to the corresponding conduction

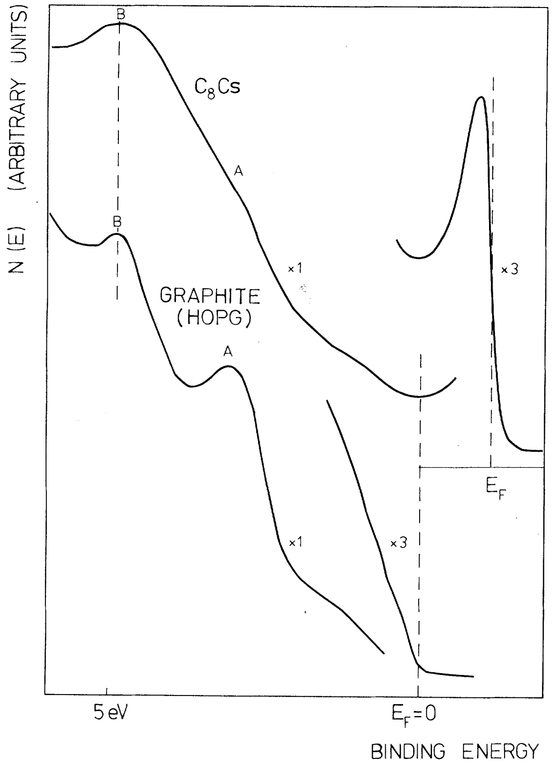

FIG. 3. UPS spectra of the C_xCs GIC's of various stages n (C_8Cs, $n=1$; $C_{24}Cs$, $n=2$; $C_{36}Cs$, $n=3$; $C_{84}Cs$, $n=7$). Normalization of the intensity and shift of energy scale as in Fig. 1.

bands in alkali metals[14-16]: In particular, the minima in the VB's of AGIC's lie 1.15, 1.2, and 1.25 eV below E_F for C_8Cs, C_8Rb, and C_8K, respectively. The corresponding values for the pure alkali metals are 1.5, 1.8, and 2.0 eV.[15,16]

These results are in contrast to some theoretical work.[3,6] However, our interpretation agrees well with other results: Inoshita, Nakao, and Kamimura[4] found potassiumlike conduction bands and a shift of E_F of 1.23 eV as a result of a semiempirical tight-binding calculation for the C_8K compound. Recently, Volpilhac[17] studied the perturbation of the graphite energy bands by introduction of alkali layers into a graphite matrix. An additional, approximately half-filled narrow band due to alkali s orbitals is shown to emerge just above the original graphite E_F.

Assuming that the free-electron model is a good approximation for the alkali metals, we can estimate the bandwidth of a hypothetic alkali conduction band within the various investigated Cs GIC's by taking into account the density variation. The calculated bandwidths for the Cs compounds are 1.45, 0.83, 0.67, and 0.41 eV for stage 1, 2, 3, and 7, respectively. The experimentally obtained values are 1.15, 0.95, 0.73, and 0.45 eV. The agreement for the stage-2, -3, and -7 compounds is very good. The reason for the deviation in the stage-1 compound might be a charge transfer from Cs to C atoms.

This idea is supported by the observed carbon 1s core-level shifts: The binding energy in the stage-1 compound decreases by 0.6 eV, taking into account a shift of E_F by 1 eV, indicating the expected charge transfer, whereas this shift is clearly smaller for the higher stages of C_xCs. According to the calculated electron density from the bandwidth, a charge transfer of 0.3 electron per Cs atom is obtained in C_8Cs. This value agrees well with Mössbauer studies[18] of C_8Cs, where the ionization of Cs was found to be 0.5 ± 0.2. If we assume the same charge transfer in C_8K and C_8Rb, the calculated bandwidth is in good agreement with the experimental value within the accuracy of the measurements. For the AGIC's, the narrow structure of the VB at E_F and the connected enhancement of the DOS do not only result in a shift of the carbon 1s core level, but also in a drastic change of its width and symmetry. The width and asymmetry of the carbon 1s peak is about 2 times larger in the compounds than in pure graphite.

It is possible to estimate an absolute value of the DOS at E_F if we assume a charge transfer of 0.3 electron/atom. We obtain a DOS at E_F of 0.19 states/(eV-C atom) for C_8Cs and of 0.17 states/(eV-C atom) for C_8K, compared to 0.23 and 0.24 states/(eV-C atom) as deduced from low-temperature specific heat measurements[19] for these compounds. These values are approximately 30 times larger than the DOS for pristine graphite. Furthermore, a schematic DOS of AGIC's can be deduced by plotting the values of the DOS at E_F obtained for all the investigated compounds versus E_F. This procedure yields a superposition of the graphite π conduction bands[5] and alkalilike s states which start 0.6 eV above E_F of pristine graphite. The DOS at E_F of $C_{84}Cs$ lies close to the DOS of the graphite conduction band; however, the DOS at E_F of the lower stages of Cs GIC's increases and for C_8Cs the DOS at E_F exceeds the graphite band by a factor of 5.

In summary, our photoemission studies provide information on the VB's of AGIC's in the following way: The DOS near E_F is considerably enhanced in AGIC's compared with pure graphite. The conduction band in the low-state AGIC's is mainly due to *s* states of the intercalated alkali metal and is only weakly influenced by the graphite host. Furthermore, the Fermi energy E_F is considerably shifted to higher energies in all the investigated AGIC's compared with pristine graphite. A reduction in the DOS at E_F with increasing stage number is observed for these compounds, and also the width of the alkali conduction band is decreased according to the reduction of the density of alkali atoms.

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Charge-Transfer and Non-Rigid-Band Effects in the Graphite Compound LiC_6

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A comparison of angle-resolved photoemission energy distributions for pure graphite and the intercalation compound LiC_6 show that considerable charge is transferred from Li to C, as expected; but the valence bands do not shift uniformly upon intercalation, in contradiction to the rigid-band approximation. Backfolded bands imposed by the two-dimensional Li superlattice are directly identified for the first time.

Research on intercalated graphite has recently entered a mature phase, motivated in part by a desire to understand in detail the novel electronic properties—high conductivity, effects of reduced dimensionality, etc.[1] The stage-1 compound LiC_6 is particularly attractive for detailed study, since the relatively simple crystal structure makes realistic band calculations feasible.[2] Many gross features of the theoretical model have been confirmed experimentally, particularly regarding integral properties of Fermi-surface (FS) electrons [$N(E_F)$,[3] Knight shift,[4] metallic reflectance,[5] and conductivity anisotropy[5]]. The in-plane part of the theoretical FS is essentially identical to that of two-dimensional (2D) graphite with E_F raised by 1.3 eV, so the good agreement between theory and experiment implies that simple rigid-band ideas are appropriate.[2] The main purpose of this Letter is to show that, on the other hand, all of the 2D graphite valence bands

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