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 LiC6

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A comparison of angle-resolved photoemission energy distributions for pure graphite and the intercalation compound LiC6 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 LiC6 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, particular-

ly 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

do not shift rigidly upon going from graphite to LiC_6. In addition, we confirm in a direct way that electrons are transferred from Li to carbon layers, as expected.

Angle-resolved photoelectron spectroscopy is extremely powerful (and easy to analyze) for quasi 2D systems such as surface states and layer crystals.[6] The component of momentum parallel to the surface $k_{\parallel}$ is conserved during photoexcitation and escape; $k_{\parallel}$ is equivalent to the in-plane crystal momentum, and is given by $\hbar k_{\parallel}$ $= (2mE_k)^{1/2} \sin\theta$, where E_k is the kinetic energy of the photoelectron and θ is the polar angle of emission. The two inequivalent in-plane directions can be distinguished on a single crystal by varying the azimuth φ as well. The 2D unit cell of LiC_6 is three times larger in area than that of graphite, because the Li atoms form a $\sqrt{3} \times \sqrt{3}$ superlattice relative to the hexagonal carbon net. In the rigid-band approximation, the in-plane part of the LiC_6 band structure is obtained from the 2D graphite bands by backfolding the latter into the threefold smaller Brillouin zone of the former, and then raising E_F to account for charge transfer.[2] Our principal conclusions are based on identifying 2D graphite valence bands in LiC_6 by observing the dispersion of valence-band features as a function of $k_{\parallel}$, i.e., θ.

Photoemission-energy distributions curves (EDC) were obtained using synchrotron radiation at the Physical Sciences Laboratory. The light flux was monochromatized by a grazing-incidence monochromator.[7] The angle-resolving photoelectron spectrometer[8] provides an angular resolution of $\pm 2.5°$ and a total energy resolution of 0.4 eV. The surface orientation was determined by 3-kV reflection high-energy electron diffraction (RHEED). The excitation geometry was fixed to give strict p polarization at 45° incidence. Normal-emission EDC's were used to obtain accurate energy locations of valence bands at the zone center. Core threshold yield spectra of LiC_6 were also obtained, by recording the total photoyield from the sample as the monochromator wavelength was scanned in the region of the Li $1s$ threshold. LiC_6 samples[5] were transferred from sealed glass ampoules to the ultrahigh vacuum (UHV) spectrometer via an argon ambient glove bag and a vacuum-interlock sample probe. Highly oriented pyrolytic graphite (HOPG) and LiC_6 were cleaved in UHV to expose fresh basal-plane surfaces. The base pressure in the spectrometer was less than 1×10^{-9} Torr.

For pure graphite we were able to distinguish

between the two principal in-plane vectors by varying φ, so that the k dispersion could be mapped along the directions $\Gamma-K$ and $\Gamma-M$ (Fig. 1). The sample orientation was determined by RHEED.[9] The upper σ and π bands of graphite have previously been determined with use of He II (40.8-eV) photons.[10] The analysis is complicated by the presence of strong final-state structures in the spectra. With synchrotron radiation, the photon-energy dependence of normal-emission spectra permits unambiguous identification of initial-state features, since they appear at fixed binding energy, whereas final-state structure occurs at fixed kinetic energy. The c-axis dispersion was estimated to be less than 0.4 eV for all bands, in agreement with theory.[11,12] The essentially two-dimensional nature of this solid is thus confirmed. The data are superimposed on a calculated band structure[13] and the overall agreement is good, especially near Γ. The weak feature which yields the nondispersing band at 3-eV binding energy might be attributable to isolated carbon atoms on the surface or to surface states.
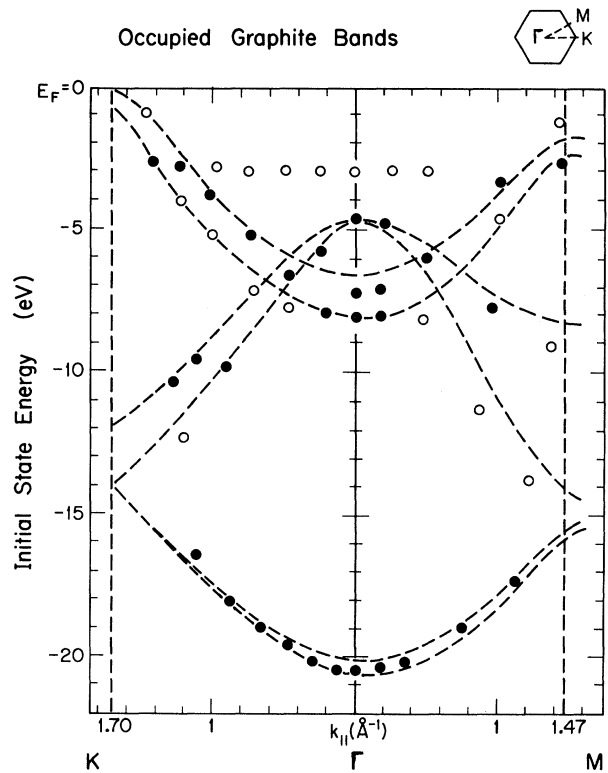

Occupied Graphite Bands

FIG. 1. E vs $k_{\parallel}$ dispersion for the 2D graphite bands compared with theory (Ref. 13), shown as dashed curves. Strong features in the spectra are marked by full circles, whereas open circles indicate weak structures.

TABLE I. Γ-point binding energies relative to E_F (in electron volts). Asterisk denotes backfolded bands. Each original graphite band contributes more than one energy level at $k = 0$ in the compound. π_1* in LiC_6 is backfolded from the K-point degeneracy of graphite (at 0 binding energy).

Symmetry label	Graphite		LiC_6	
	Expt.	Theory[a]	Expt.	Theory[b]
π_1*	0	0	-0.5 ± 0.3	-1.3
$\sigma_{2,3}$	-4.6 ± 0.3	-4.7	-0.5 ± 0.4	-5.9
π_1	-7.2 ± 0.3	-6.6	-9.3 ± 0.3	-9.3
π_1	-8.1 ± 0.3	-8.2		
$\sigma_{2,3}*$	$\cdots$	$\cdots$	-13 ± 0.5	-13.3
$\sigma_1*, \sigma_{2,3}*$	$\cdots$	$\cdots$	$\cdots$	-14.9
σ_1*	$\cdots$	$\cdots$	-15.2 ± 0.5	-15.4
σ_1*	-20.6 ± 0.3	-20.1	-22.5 ± 0.4	-21.8
σ_1*		-20.7		

[a]Ref. 13.   [b]Ref. 2.

The experimental and calculated binding energies of the graphite bands at Γ are listed in Table I.

For LiC_6, RHEED gave a powder-averaged azimuthal pattern and hence we could not distinguish $\Gamma - K$ from $\Gamma - M$.[14] Figure 2 gives a sample of the EDC's obtained. The large dispersion of the features occurring at -10 and -24 eV with $\theta = 0°$ allows us to identify them as graphitelike bands by matching with the dispersion of bands in graphite. The feature just below E_F can be attributed to a backfolded band since it decreases in intensity as we approach the edge of the first
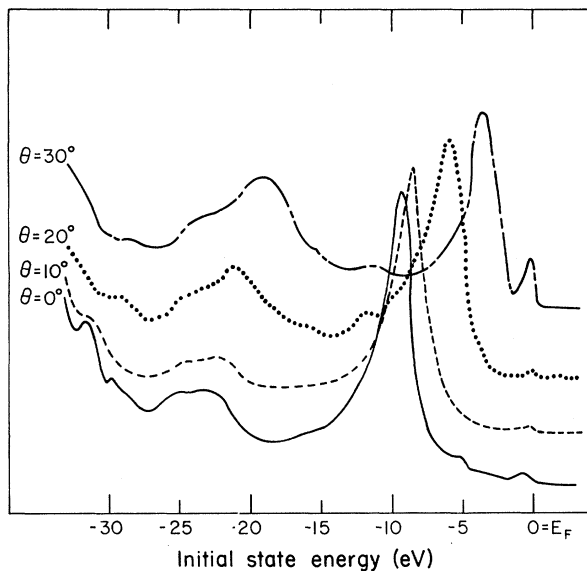

FIG. 2. EDC's for LiC_6 at several polar angles θ and $\hbar\omega = 40$ eV. The small feature near E_F is identified as a backfolded band by its θ-dependent intensity (see text).

zone $(0° < \theta < 20°)$ then grows again as we enter the second zone $(\theta = 30°)$. Backfolded bands generally appear as weak features in the spectra ($< 5\%$ of the original band intensity). All bands are found to shift to higher binding energy relative to graphite, by amounts varying from 0.5 to 2.1 eV over the range studied.

In Fig. 3 we align two normal-emission EDC's with the theoretical band structure. Peaks corresponding to valence-band emission should line up with the theoretical curves at Γ. We distinguish "original" and backfolded bands via solid and dashed curves and arrows. The agreement is remarkably good, except for the uppermost band. This is more obvious from Table I, to which we have added the experimental and theoretical Γ-point energies for LiC_6. The results confirm within experimental error the predicted nonrigid shift relative to pure graphite $(\sigma_{2,3}\pi_1, \sigma_1)$, as well as the occurrence of symmetry-induced bands uniquely ascribable to the $\sqrt{3} \times \sqrt{3}$ superlattice $(\sigma_{2,3}*, \sigma_1*)$. The nonrigid part of the band shift is significant (~ 1 eV) and implies appreciable Li interaction even with the sp^2 electrons. These effects are usually ignored.[15] The direct observation of zone folding is significant in the context of the long-standing controversy over the Raman spectra,[16] as well as other symmetry-related considerations which affect the electronic properties.[17]

In light of this generally excellent agreement, we were surprised at the large discrepancy in the uppermost band π_1*. This band is backfolded from the K point in graphite, and according to Holzwarth, Rabii, and Girifalio[2] shifts down by
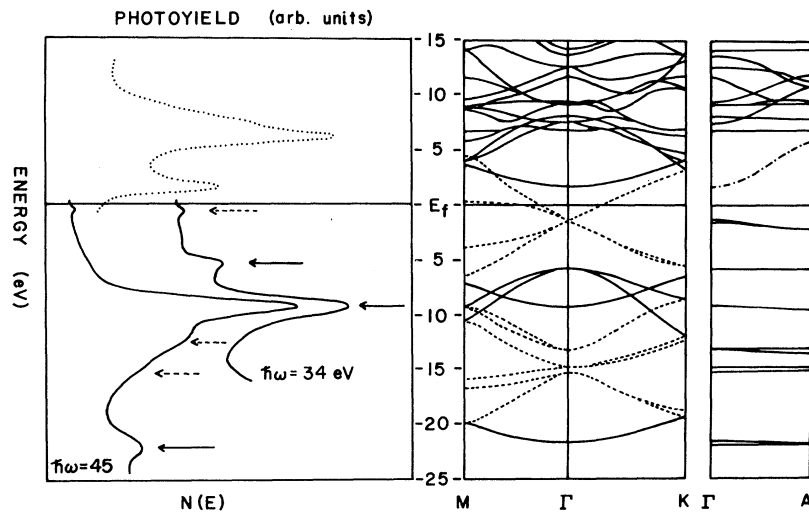
FIG. 3. Comparison of normal-emission and core-threshold photoyield spectra with the calculated band structure (Ref. 2) for LiC_6. For occupied bands within M-Γ-K, original graphite bands are denoted by full lines, backfolded bands by dashed lines. In the normal-emission spectra, graphitelike and backfolded features are indicated by full and dashed arrows, respectively. The strongly dispersing vacant band denoted by the dash-dotted line is derived mainly from Li $2s$ orbitals.

1.3 eV to accommodate the charge transferred from Li. Our data put this point much closer to the Fermi energy, implying that the Fermi surface of LiC_6 must be considerably different than would have been predicted from a rigid shift of the graphite bands. In support of our assignment of this problematic feature is the observation that the band shift is systematically smaller the closer the band is to the Fermi energy: 1.9 eV for σ_1; 2.1 eV for π_1; 0.9 eV for $\sigma_{2,3}$; and 0.5 eV for the original K-point degeneracy ($\pi_1{}^*$ in LiC_6).

The transfer of electrons from Li to C is confirmed from the band shifts discussed above. In addition, the Li $1s$ binding energy is found to be 56.8 eV, as compared with 54.86 eV in Li metal[18] and 57.6 eV in LiF.[19] If we allow for somewhat greater relaxation effects in LiC_6 than in LiF, this confirms that the Li in LiC_6 is essentially Li^+. Finally, the total yield from photoexcitation of Li $1s$, shown as the upper left panel in Fig. 3, exhibits two peaks which align with density-of-final-states maxima in the calculated bands (dash-dotted band along Γ–A, derived from empty Li $2s$ orbitals). Such a yield spectrum mimics the Li $1s$ absorption spectrum and thus reflects the unoccupied states local to Li (Ref. 20). The agreement with experiment, and the absence of strong absorption near E_F, confirm that the Li $2s$ band is essentially unoccupied.

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Donor-Acceptor Recombination Spectra in CuCl

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This Letter reports donor-acceptor pair spectra in CuCl crystals. A simple neutral-donor, neutral-acceptor complex does not explain the data. Recent calculations have predicted an O⁻⁻ level near the conduction-band minimum. It is this level which is speculated to be the source of electrons for the highly conducting state of this potentially excitonic superconducting material. The photoluminescence results reported in this paper do not confirm the O⁻⁻ level but would be consistent with its existence.

The optical properties of CuCl have been studied by a number of investigators over a period of nearly twenty years,[1-5] investigations which have established the free-exciton structure as well as the energy band structure at the center of the Brillouin zone. In the earlier work, some extrinsic spectral structure was also observed including transitions associated with neutral acceptor bound excitons.[5] Recently, a series of very interesting experiments on CuCl have revealed that the magnitude of its magnetic susceptibility varies over a wide range, from ~-10^{-6} to -1, under controlled experimental conditions. For example, Brandt *et al.*[6] have shown that CuCl samples, when cooled at a rate of 20 °K/min under a hydrostatic pressure of 5 kbar, undergo a series of

transitions from a state of weak diamagnetism to one of strong diamagnetism ($\kappa \sim -1$) at a temperature of approximately 170 °K. The transition to a strongly diamagnetic state was accompanied by a sharp increase in electrical conductivity. Similar experiments were also performed by Chu *et al.*,[7] in which a strong diamagnetism ($\kappa \sim -0.1$) was also observed. Although still a conjecture, there is a nevertheless a strong possibility that CuCl, and perhaps related materials, may be capable of supporting a supercurrent at elevated temperatures and pressures. These experiments have stimulated a renewed interest in CuCl, its electrical and optical properties, and its energy band structure. The energy band structure of CuCl has been recently calculated by Kunz, Weid-