

Three-Dimensional Energy Band in Graphite and Lithium-Intercalated Graphite

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Angle-resolved inverse photoemission with tunable photon energies has been used to map out the unoccupied bands of graphite and lithium-intercalated graphite. At the Brillouin zone center the bottom of the lowest band is found at 4.0 ± 0.5 eV above the Fermi level in graphite. This band shows strong dispersion normal to the basal plane in excellent agreement with recent self-consistent band-structure calculations. A similar three-dimensional band is found in lithium-intercalated graphite shifted 3 eV to lower energy.

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Graphite has been a prototype two-dimensional solid. Band-structure calculations throughout several decades¹ gave a simple picture of the electronic structure of graphite in terms of bonding and antibonding combinations of the $2s$ and $2p$ orbitals of carbon (see Fig. 1). All states up to about 10 eV above the Fermi level were thought to be two dimensional, i.e., very little band dispersion was expected perpendicular to the basal plane. Recently, three-dimensional states have been predicted²⁻⁴ in the gap between the bonding and antibonding states at the Brillouin zone center. So far there exists no experimental evidence for such states. These three-dimensional states are concentrated in the space between the carbon layers and, therefore, play an important role for intercalated graphite, a field of very active research.⁵ In particular, when alkali metals are intercalated (e.g., LiC_8) their outermost s states should interact with the graphite interlayer states and the question arises whether or not the alkali states preserve their identity in the intercalate.^{3,6} Recent self-consistent band-structure calculations^{2,3} predict a three-dimensional σ band with a charge density concentrated mainly between the carbon layers. Since the bottom of this band lies below the vacuum level it cannot be probed by electron spectroscopies⁷ and it was not seen by optical spectroscopies either.

Momentum-resolved bremsstrahlung spectroscopy (inverse photoemission) observes direct optical transitions of incoming electrons from free-electron-like states above the vacuum level into unoccupied states of the sample (see wavy lines in Fig. 1). By employing different electron and photon energies we can change the momentum

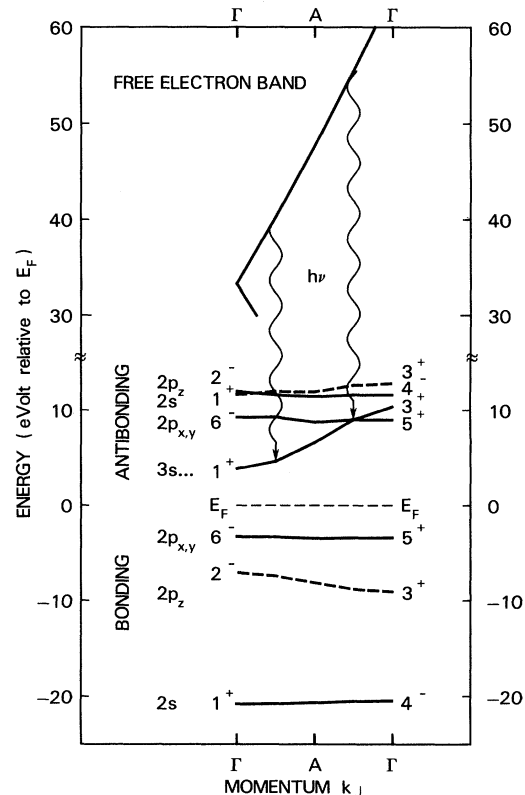


FIG. 1. Band dispersion of graphite normal to the basal plane at $k_{\parallel} = 0$ after Ref. 2. The bands are unfolded into a double Brillouin zone (Ref. 8). The two-dimensional bonding and antibonding $2s$ and $2p$ states show little dispersion, whereas the three-dimensional $3s$ -derived interlayer band disperses strongly. The wavy lines show radiative transitions from a free-electron-like initial band into the final states above the Fermi level observed by inverse photoemission. The momentum k_{\perp} is tuned by changing the photon energy $h\nu$.

k_{\perp} perpendicular to the surface. In off-normal incidence of the electrons we can map the band structure for $k_{\parallel} \neq 0$.

The experiments were carried out with use of a Seya-Namioka monochromator and a position-sensitive device for photon detection, and a Pierce-type electron gun as the electron source.⁹ Photon energies range from 10 to 50 eV with a total energy resolution of ≥ 0.3 eV and a momentum resolution of 0.1 \AA^{-1} . Samples of highly oriented graphite and intercalated graphite were cleaved *in situ* to expose clean basal-plane surfaces. The intercalated samples were introduced from sealed glass ampules into the vacuum system through a sample interlock via a glove bag under helium atmosphere.

Figure 2 shows spectra for graphite and LiC_6 taken in normal incidence relative to the basal plane for initial-state energies E_i between 22 and 48 eV. All graphite spectra show a prominent

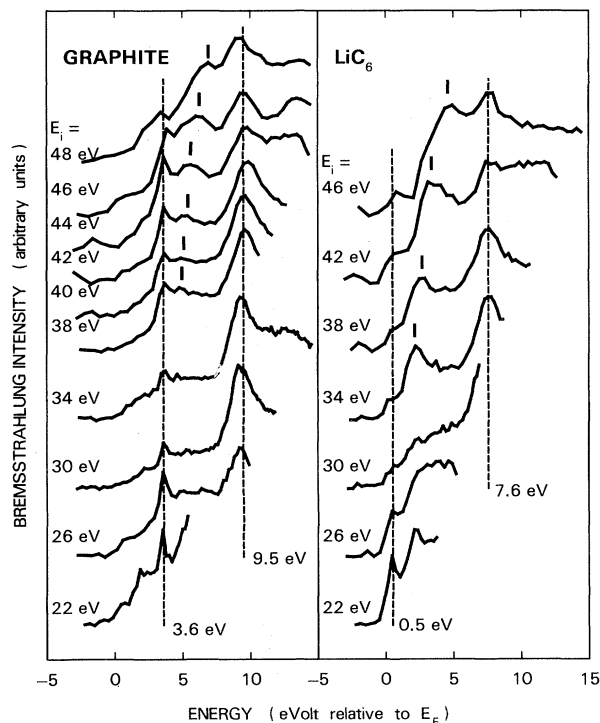


FIG. 2. Inverse photoemission spectra (photon intensity vs energy of the empty state, $E_i - h\nu$) for graphite and lithium-intercalated graphite in normal incidence for initial state energies E_i between 22 and 48 eV above E_F . The peaks corresponding to the three-dimensional band disperse with photon energy $h\nu$ and are tick marked. The stationary structures at 9.5 and 7.6 eV, respectively, are due to transitions into two-dimensional empty $2p_{x,y}$ states.

peak around 9.5 eV arising from transitions into the $2p_{x,y}$ -derived states at Γ . This nondispersing band is readily identified with the antibonding σ band (Γ_6^- symmetry at $k=0$) which is derived from empty antibonding atomic $2s$ and $2p_{x,y}$ wave functions. Recent calculated values for this band are 9.0 and 7.2 eV above E_F in Refs. 2 and 4, respectively. In addition to this nondispersing two-dimensional state the spectrum for $E_i = 48$ eV shows a peak at ~ 7 eV which can be seen dispersing down to ~ 5 eV (tick marks in Fig. 2) at lower photon energies. This is clear evidence for the predicted three-dimensional interlayer band in graphite.^{2,3} To compare the experimental data with theory, we assumed a free-electron-like initial-state band (Fig. 1) with a bottom at the valence-band minimum. In Fig. 3 we compare the resulting k_{\perp} dispersion (solid dots) with the calculation of Holzwarth, Louie, and Rabi² (solid curve). An extrapolation of the experimental band dispersion yields a value of 4.0 ± 0.5 eV for the bottom of this band. The calculated band has Γ_1^+ symmetry at $k=0$,^{2,4} is derived from empty carbon $3s$ states, and is predicted to have charge contours clustered in the interlamellar space³ (hence the appellation "interlayer state"). The calculated positions of the Γ_1^+ minimum are 3.8 and 3.4 eV in Refs. 2 and 3, respectively. Previous angle-integrated inverse photoemission data have observed structures in the energy range of

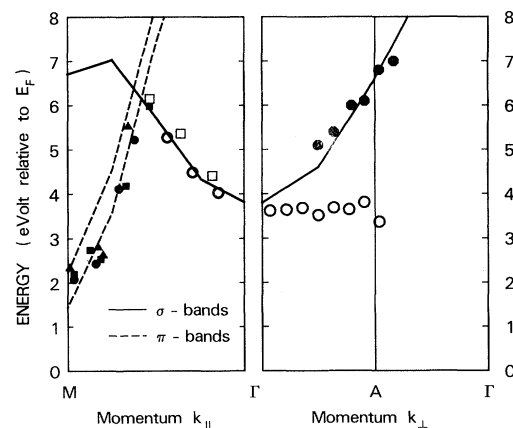


FIG. 3. Comparison of experimentally determined energy bands for graphite (symbols) with the calculations of Ref. 2 (lines). The right half shows the dispersion $E(k_{\perp})$ of the three-dimensional band; the left half shows the two-dimensional dispersion $E(k_{\parallel})$ for the π bands (dashed) and for the bottom of the three-dimensional band (full). The different symbols denote different initial-state energies (circles, 28 eV; squares, 40 eV; and triangles, 50 eV).

the three-dimensional σ band but they were interpreted in terms of π bands¹⁰ and matrix-element effects.¹¹ The open circles in Fig. 3 correspond to the peak at 3.6 eV seen independent of photon energy in Fig. 2. It could be due to nondirect transitions into the high density of states at the bottom of the band, or it could be a surface-state split-off from the bottom of the band. Both interpretations give a lower limit for the Γ_1^+ minimum of 3.6 eV. For $k_{\parallel} \neq 0$, as well, this structure follows the dispersion calculated for the bottom of the σ interlayer band (open symbols and full line in the left panel of Fig. 3).

The bremsstrahlung spectra for lithium-intercalated graphite (right half of Fig. 2) parallel those for graphite, but are shifted to lower energy. In LiC_6 a nondispersing peak occurs at 7.6 eV (right panel of Fig. 2), suggesting that it originates in the same σ band as in graphite. The σ band, which is localized on the graphite layers, should be weakly affected by the 10% increase in layer spacing between graphite and LiC_6 , or by the presence of Li in the interlayer region. Thus a rigid-band approach should be a reasonable basis for comparing the σ energies in the two materials. Photoemission experiments^{12,13} indicate ~ 1.6 -eV increase for E_F , which is compatible with a rigid-band interpretation of the σ shift within the experimental accuracy. The Fermi-level raising results from the filling of the graphite band structure with the Li 2s electron. A band with three-dimensional dispersion occurs also in LiC_6 (tick marks, right panel of Fig. 2) and it appears to have about the same k_{\perp} dispersion as the comparable peak in graphite. We can therefore deduce that, relative to the respective Fermi levels, the band is shifted ~ 3 eV down in LiC_6 compared to graphite, a greater shift than for the nondispersing σ band whose charge is localized on the graphite layers. We interpret this extra 1-eV non-rigid-band shift as a measure of the hybridization between Li(2s) and carbon interlayer states. These lie close to each other in energy at infinite separation, both have Γ_1^+ symmetry, and both are concentrated about interstitial sites in the graphite structure. Thus substantial hybridization is expected. The calculated values for the interlayer band minimum are between 1.3 and 2.2 eV above E_F ,^{3,6} which is higher than our value of 0.5 eV for the nondispersing peak at the bottom of the band (Fig. 2).

Li(1s) photoelectron yield spectra¹² were interpreted as evidence for states with substantial Li character at ~ 2 eV above E_F . This experiment

differs from ours in several respects: (i) Mainly states near the Li cores are probed, (ii) states are probed in the presence of a Li(1s) core hole, (iii) states with different momenta are sampled simultaneously, and (iv) predominantly states with p -like symmetry are selected. These results are compatible with our band-structure determination if we assign the 2-eV peak to transitions into the center of gravity of the interlayer density of states. The bottom of the interlayer band is s like and will not contribute much to the Li(1s) absorption.

In Fig. 4 the $E(k_{\parallel})$ dispersion is sampled by changing the angle of incidence θ of the electrons relative to the surface normal ($k_{\parallel} = k \sin\theta$). Different initial-state energies correspond to different k_{\perp} and give nearly identical $E(k_{\parallel})$ dispersions. This proves the two-dimensional character of the π bands. The experimental $E(k_{\parallel})$ dispersion is compared with the calculation² for the antibonding π bands along the ΓM direction (left panel of Fig. 3) after folding back into the first Brillouin zone. The experimental value for the π -band extremum at M is 2.0 ± 0.3 eV, in good agreement with the value of 1.7 eV given by Dose, Reusing, and Scheidt.¹⁰ Extra features in Fig. 4 (e.g., the peak at ~ 2 eV) are attributed to the other azimuthal directions induced by the rotational disorder of our samples.

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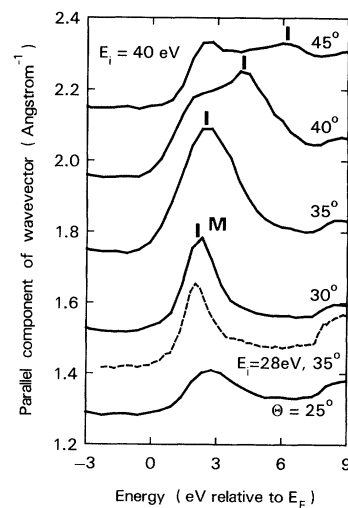


FIG. 4. Inverse photoemission spectra showing the two-dimensional dispersion of the antibonding π bands (tick marks).

tabulated energy eigenvalues of the graphite band structure. The able help of J. J. Donelon and A. Marx is acknowledged. The work at the University of Pennsylvania was supported by the National Science Foundation—Materials Research Laboratory Program, Grant No. DMR 79-23647.

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