Evidence for Interlayer Band Shifts upon Lithium Intercalation in Graphite from Inelastic X-Ray Scattering

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The dielectric function $\epsilon(\mathbf{q},\omega)$ of Li-intercalated graphite (LiC_6) with $\mathbf{q} \parallel c$ axis was deduced from inelastic x-ray scattering data and compared with $\epsilon(\mathbf{q},\omega)$ of pristine graphite. A displacement and broadening of the first peak of $\mathrm{Im}\epsilon(\mathbf{q},\omega)$ upon intercalation was found, which we attribute to a 2-eV shift of the "metal" σ state of LiC_6 to lower energies relative to the σ-type interlayer state of graphite.

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First-stage Li-intercalated graphite (LiC_6) is one of the alkali-metal–graphite intercalation compounds whose electronic structure has been thoroughly investigated both experimentally[1-6] and theoretically.[7-10] It is commonly accepted that, upon intercalation of Li, the electrons are completely transferred from the Li 2*s* states to previously empty carbon π states. This charge transfer can be understood within the framework of the so-called rigid-band model, where the in-plane part of the LiC_6 band structure is the result of backfolding of the 2D bands of graphite into the smaller Brillouin zone of LiC_6. Nevertheless, the full understanding of the electron structure of alkali-metal–graphite intercalating compounds also needs consideration of changes of the band structure beyond the rigid-band model, both due to the existence of Li ions between the graphite layers and as a result of the altered stacking of graphite layers. The so-called interlayer states[8] of graphite are important candidates for those changes since strong hybridization with Li 2*s* states is rather likely. Angle-resolved inverse-photoemission (ARIPE) results[4] on LiC_6 and graphite have corroborated this assumption.

It is the aim of this Letter to present further evidence for nonrigid behavior of the LiC_6 conduction bands by comparison of inelastic x-ray–scattering spectroscopy (IXSS) data of LiC_6 with those of pristine graphite. In contrast to electron-energy-loss spectroscopy,[5] measurements with $\mathbf{q} \parallel c$ axis could be performed with IXSS, so that a new spectroscopic access to the interlayer states was opened via dipole-allowed transitions from π states to the interlayer states.

IXSS measures the dynamic structure factor $S(\mathbf{q},\omega)$ and the imaginary part of the inverse dielectric function, $\mathrm{Im}\epsilon^{-1}(\mathbf{q},\omega)$, both on an absolute scale, by utilization of the oscillator strength sum rule,[11] so that $\epsilon_1(\mathbf{q},\omega) \equiv \mathrm{Re}\epsilon(\mathbf{q},\omega)$ and $\epsilon_2(\mathbf{q},\omega) \equiv \mathrm{Im}\epsilon(\mathbf{q},\omega)$ can be obtained by means of Kramers-Kronig transformation. It is the well-known relation between $\mathrm{Im}\epsilon(\mathbf{q},\omega)$ and symmetry projection of the joint density of states (DOS) that brings about the desired band-structure information.

The IXSS measurements of $S(\mathbf{q},\omega)$ with 0.8-eV resolution were performed by use of synchrotron radiation from the DORIS storage ring at DESY, monochromatized to an energy of 8 keV by a Ge(311) double-crystal setting. The scattered radiation was analyzed by means of a spherically bent Si(444) crystal. Details of the experimental setup and of data processing are described elsewhere.[11,12] The graphite sample was a highly oriented pyrolytic graphite (HOPG) disk of 1.3-mm thickness. The LiC_6 sample of 2-mm thickness and $20 \times 30\text{-mm}^2$ lateral dimension was obtained by a liquid-phase reaction under clean Ar atmosphere with HOPG. Stage and homogeneity of the LiC_6 sample was controlled by energy-dispersive x-ray diffraction both before and after the experiment. The LiC_6 sample was transferred from argon-filled glass ampules to the scattering chamber via an argon ambient glove bag and then held at 10^{-6} Torr. The bright golden surface did not deteriorate during the six days of the experiment.

The sequence of presentation of the results is as follows: In the first place, carbon 1*s* core-excitation spectra (CES) will be presented, displayed together with angle-resolved x-ray emission spectroscopy (ARXES) results in order to fix the Fermi level and to demonstrate the nearly rigid-band behavior of the involved conduction bands. In the second place, the strong changes of the valence-electron excitation spectra with $\mathbf{q} \parallel c$ will be discussed in terms of hybridization of the interlayer states with states originating from Li 2*s*.

In Fig. 1 the carbon 1*s* CES's of LiC_6 and HOPG are compared. Within the limits of a 2D representation of the band structure, and with utilization of dipole selection rules, the $\mathbf{q} \parallel c$-axis spectra and the $\mathbf{q} \perp c$-axis spectra reflect a symmetry-projected partial DOS of π^* states

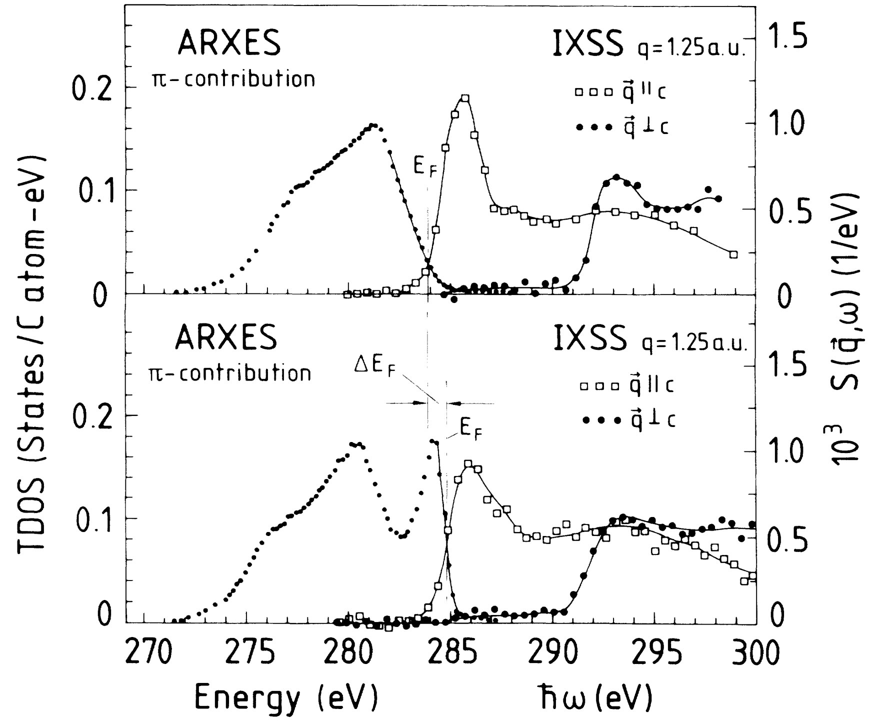


FIG. 1. Right-hand part, right-hand scale: C 1*s* core contribution to $S(\mathbf{q},\omega)$ of HOPG (upper part) and LiC$_6$ (lower part), with $\mathbf{q} \parallel c$ axis (open squares) and $\mathbf{q} \perp c$ axis (filled circles). Left-hand part, left-hand scale: π contribution of the C *K* x-ray emission band for graphite (upper part) and LiC$_6$ (lower part), according to Ref. 6. E_F, estimated position of the Fermi level; ΔE_F, Fermi-level shift.

and σ^* states, respectively.[12] Together with the IXSS data the corresponding π contribution to the ARXES spectra[6] is displayed. The intersection of ARXES spectra with the IXSS spectra indicates the Fermi energy E_F relative to C 1*s*.

Hence a shift of E_F to higher energies by $\Delta E_F = 1.0 \pm 0.3$ eV follows upon Li intercalation, if we ascribe the measured[2] lowering of the C 1*s* binding energy, $\Delta E_B = 0.8$ eV, solely to a change of the core-hole relaxation. Otherwise, an unknown fraction *p* of ΔE_B had to be added to ΔE_F. We attribute the first pronounced peak in the $\mathbf{q} \parallel c$ CES to regions of high DOS of unoccupied π states in graphite (π_2 in Fig. 2 near *M*) and π-originated states in LiC$_6$, respectively. We explain the reduction of peak height and a small shift (≈ 0.5 eV) of the peak position to higher energies (contrary findings in electron-energy-loss spectroscopy[5] must be left unexplained) as a result of the filling of part of the graphite π states by electrons transferred from Li 2*s* states. Hence our results are consistent with a nearly rigid-band behavior of graphite π states upon intercalation. We interpret the steep rise of the $\mathbf{q} \perp c$ CES as brought about by the onset of the contribution to the DOS of unoccupied graphite σ states (σ_5 and σ_6 in Fig. 2) and LiC$_6$ σ-derived states, respectively, with appropriate symmetry.[11] The inflection points of this rise are exactly at the same position for HOPG and LiC$_6$, so that this σ-DOS feature has not been shifted by more than $p\Delta E_B$ upon Li intercalation, an indication of a nearly rigid-band behavior of those graphite σ states that have a strong overlap with C 1*s* states. The σ-type interlayer states σ_4 in Fig. 2 do not contribute appreciably to the C 1*s* CES, since their overlap with C 1*s* can be neglected. The vanishing

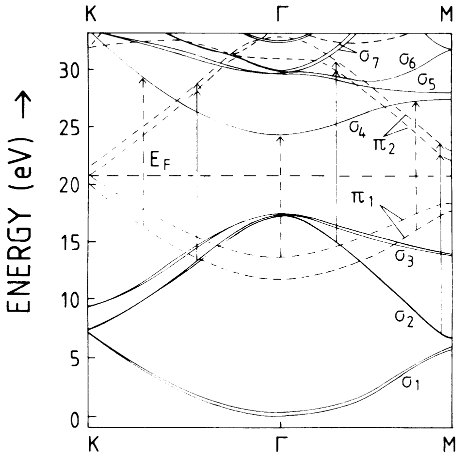


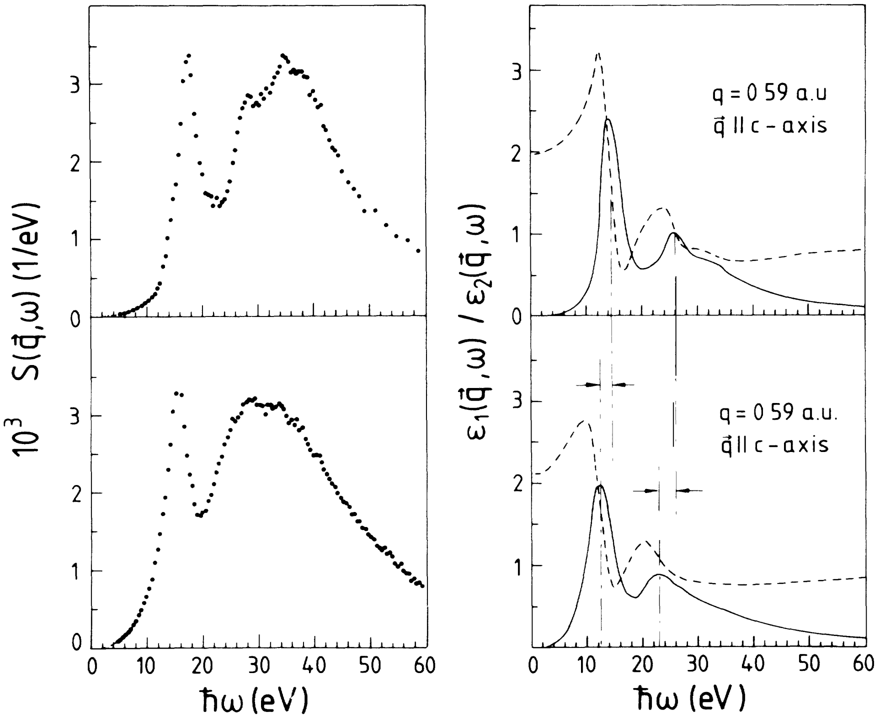
FIG. 2. Partial energy-band structure of graphite according to Ref. 13. Solid curves: σ bands; dashed curves: π bands. The arrows indicate some dipole-allowed vertical transitions for $\mathbf{q} \parallel c$ axis.

of the peak at 293 eV in the $\mathbf{q} \perp c$ spectrum of graphite upon intercalation can be interpreted as due to σ-band folding.

The normalized $S(\mathbf{q},\omega)$ spectra of HOPG and $\mathrm{LiC_6}$ with $\mathbf{q} \parallel c$ axis ($q=0.59$ a.u.) are presented in Fig. 3(a); the real (ϵ_1) and imaginary (ϵ_2) parts of $\epsilon(\mathbf{q},\omega)$ are presented in Fig. 3(b). The main feature in the ϵ_2 spectra of graphite is the strong peak at 14.6 ± 0.2 eV which is shifted by 2.0 ± 0.4 eV to 12.6 ± 0.2 eV upon Li intercalation. The FWHM of this peak increases from 4.5 ± 0.2 eV in HOPG to 6.0 ± 0.2 eV in $\mathrm{LiC_6}$. In discussion of these findings in terms of the band structure, all transitions can be considered as vertical, since $q \approx 2\overline{\Gamma A}$.

On the basis of dipole selection rules it was deduced in Ref. 12 that the first peak of $\epsilon_{2\parallel}$ in graphite is composed of two contributions which are only slightly separated in energy so that they could not be resolved experimentally. The one peak contribution at higher energy transfer (≈ 16.5 eV) is due to vertical transitions between the σ_2 band and the nearly parallel π_2 band (solid arrow in Fig. 2). The second contribution at lower energy transfer ($\simeq 13.5$ eV) originates from vertical transitions (dashed arrow in Fig. 2) between the π_1 band and the nearly parallel σ-type interlayer band (σ_4 in Fig. 2). This transition contributes to $\epsilon_{2\parallel}$ because of the considerable extension of the π states into the interlayer region. A double-peak structure of the above type was also predicted in Ref. 10.

Hence the shift and broadening of the first $\epsilon_{2\parallel}$ peak upon intercalation can be explained as follows: The energy of the $\sigma_2 \rightarrow \pi_2$ transition remains roughly the same because of the nearly rigid-band behavior both of the σ_2 band (see Ref. 1) and of the π_2 band (see our CES results). In contrast, the energy of the $\pi_1 \rightarrow \sigma$-type interlayer state (σ_4) transition is shifted by at least 2 eV to lower values, since the "metal" σ band of $\mathrm{LiC_6}$ (notation according to Ref. 10) is by 2 eV lower in energy than the σ-type interlayer state of pristine graphite, from which it originates, possible because of strong hybridization with the Li metal $2s$ band,[9] whereas the π_1 band behaves nearly rigidly (see Ref. 1). In terms of the hybrid point of view, the measured energy shift of at least 2 eV must be considered as a measure of the degree of hybridization. Fauster *et al.*[4] have found in ARIPE the corresponding energy shift to be 1.4 eV; calculations of Holzwarth, Louie, and Rabii[7] have determined the shift at Γ to be 1.6 eV, resulting in a shift of ≈ 2 eV of corresponding peaks in $\epsilon_{2\parallel}$ (Ref.10) in excellent agreement with our measurements.



(a) (b)

FIG. 3. (a) IXSS-measured $S(\mathbf{q},\omega)$ for $\mathbf{q} \parallel c$ axis ($q=0.59$ a.u.) of HOPG (upper part) and $\mathrm{LiC_6}$ (lower part). Small dots at low energy transfer indicate the less-reliable part of the spectrum because of heavy superposition by the Rayleigh line. (b) $\epsilon_1(\mathbf{q},\omega)$ (dashed curve) and $\epsilon_2(\mathbf{q},\omega)$ (solid curve) of HOPG (upper part) and $\mathrm{LiC_6}$ (lower part). Peak shifts upon intercalation are indicated.

The shift by 3 eV of the second peak in the $\epsilon_{2\parallel}$ spectrum to lower energies upon intercalation could be explained as due to a shift to lower energies upon intercalation of the σ-type conduction bands with strong k_z dispersion, which were found by Tatar and Rabii[14] in their band calculations of graphite to be parallel to the "rigid" π_I bands.[12]

In conclusion, we have directly measured for the first time the dielectric function $\epsilon(\mathbf{q},\omega)$ with $\mathbf{q} \parallel c$ axis of graphite and LiC$_6$. Thus we could make accessible by dipole transition rules transitions from π states to σ-type interlayer states utilizing their considerable spatial overlap. We could establish the energy shift of the interlayer states of graphite upon intercalation in agreement with theoretical predictions and ARIPE results.

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