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Unoccupied electronic states of graphite as probed by inverse-photoemission and tunneling spectroscopy

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The unoccupied electronic bulk and surface states of graphite are probed by inverse photoemission at $h\nu=9.7$ eV and by tunneling spectroscopy, and the results from each method are found to agree very well with each other. In particular, π^* bands at the bulk Q point are found at $E_F+1.7$ eV. Extrinsic surface states (or defect states) are found around $E_F+2.5$ eV, which can be quenched by activated hydrogen or oxygen and by water at low temperatures, but are also dependent on surface preparation. In contrast, the feature at $E_F+3.5$ eV is left unaffected, questioning an interpretation in terms of intrinsic surface states. Rather, we associate it with the bottom of the three-dimensional interlayer band.

I. INTRODUCTION

The unoccupied electronic structure of graphite and its intercalated compounds has recently attracted considerable attention.[1-7] Holzwarth *et al.*[1] and Posternak *et al.*[2] predicted interlayer states with a strong energy dispersion $E(\mathbf{k})$, $\mathbf{k}\,||\,\hat{\mathbf{c}}$, which indicated a nonnegligible electronic interaction between the graphite layers, i.e., a rather unexpected result for a two-dimensional layered material. Employing inverse-photoemission spectroscopy with tunable photon energy, Fauster *et al.*[4] actually observed the interlayer band and found an energy dispersion in agreement with the calculations.[1,2] In addition, a nondispersing spectral feature appeared in all the inverse-photoemission spectra at $E_F+3.6$ (E_F denotes the Fermi level), which Fauster *et al.*[4] interpreted as either (i) nondirect transitions into a high density of states at the bottom of the interlayer band, or (ii) a surface-state split-off from this band. Consecutively, Posternak *et al.*[5] performed a thin-film calculation on graphite, and predicted a surface-state band which extends about three layers into the bulk, and is split-down by 0.3 eV from the bottom of the interlayer band in agreement with the inverse-photoemission feature[4] at $E_F+3.6$ eV. An experimental proof of this surface-state assignment is, however, still lacking. One possibility would be quenching of the inverse-photoemission feature at 3.6 eV with exposure of the clean graphite surface to various (activated) gases, as was successfully used to identify unoccupied surface states on the noble-metal surfaces Ag(110),[8] Ag(100),[9] Cu(110),[10] and Au(110).[11] Another possibility has recently been suggested by Selloni *et al.*,[7] namely, to measure I-V curves (so-called tunneling spectra) with the scanning tunneling microscope (STM) as demonstrated by Binnig *et al.*[11] Unoccupied bulk and surface states may be distinguished by considering tunneling spectra at different tip-surface separations. Here, we report I-V curves and normal-incidence inverse-photoemission data on clean and exposed graphite.

II. EXPERIMENT

For the inverse-photoemission experiments, the sample was bombarded with electrons from a custom-built electron gun based on the design of Erdman and Zipf[12] and equipped with a BaO cathode. The divergence of the incident electron beam was measured to be $\Delta\theta\leq 5°$, which resulted in an uncertainty of $k_{||}$, the wave vector parallel to the surface, of $\Delta k_{||}<0.1$ Å^{-1}. The intensity of the outcoming photons was filtered at $h\nu=9.7$ eV and monitored with a Geiger-Müller–type counter[13] as a function of primary electron energy. The overall energy resolution (electrons and photons) was 0.7 eV as determined from the Fermi-level onset of a metallic reference sample in electric contact with the graphite sample.[13] The vacuum in the spectrometer chamber which also contained Auger-electron spectroscopy and ultraviolet photoemission (He I, He II) facilities was in the low-10^{-10}-Torr range. Highly oriented pyrolytic graphite (HOPG) from Union Carbide was introduced into the vacuum through an interlock system, and several graphite layers were peeled off *in situ* with a knife to obtain a clean surface. Polycrystalline graphite was prepared by air-brushing Aquadag onto a Ta foil, which was then cleaned *in vacuo* by heating to ≈ 700 °C. In both cases, only a carbon Auger signal could be observed. Hydrogen, oxygen, and water could be leaked into the system, and activated by a hot filament. For the water adsorption, the graphite sample was liquid-nitrogen-cooled to 110 K as monitored by a thermocouple.

The tunneling spectroscopy was performed with a STM described elsewhere.[14] HOPG from the same batch as used for inverse photoemission was cleaved under 1 atm of N_2 and introduced into the STM chamber with a base pressure of 10^{-8} Torr. The delicate layer structure of the material made *in vacuo* cleavage difficult, since exfoliated layers caused "whiskering" effects. The type of tunneling spectrum presented here differs from the spectra recently measured[11] for Ni(100), Si(111)-(7×7), oxygen on Ni(100), etc. In the present experiments the tip-sample distance s

was kept constant, while the gap voltage (0–5 V) was ramped up and down at a frequency of 180 Hz, and the feedback loop regulated on the mean current level (typically 10 nA) by setting the low-pass filter well below the ramp frequency. The I-V characteristics were obtained by averaging over several hundred sweeps, and numerical differentiation produced the tunneling spectrum, i.e., the (dI/dV)-versus-V characteristics at constant s. An energy resolution of 0.1 eV as an upper limit is estimated from field-emission energy-distribution curves.[15] Both polycrystalline silver and tungsten tips were used, giving essentially the same results, so that we are confident the spectral features reported are representative of the sample.

III. RESULTS AND DISCUSSION

In Fig. 1 we present normal-incidence ($k_{\parallel}=0$) inverse-photoemission spectra of graphite at $h\nu=9.7$ eV. Four different cases are shown and will now be discussed in detail. In curve (a) we note two features in the spectrum of polycrystalline graphite. A broad shoulder denoted π^* is located at $E_F+(1.7\pm0.1)$ eV and a weaker structure denoted G may be discerned at $E_F+(3.5\pm0.1)$ eV. The energy uncertainty of ±0.1 is due to the determination of E_F from a metallic reference sample in contact with the graphite. This inverse-photoemission spectrum (a) should be compared with the first such measurements[16] on well-ordered epitaxially grown graphite film which were, however, measured in an angle-integrated mode. The same two features were observed, although with a different intensity ratio,[16] which we attribute to possible annealing effects of our polycrystalline sample, i.e., an ordering perpendicular to the surface so that **k** averaging owing to the polycrystalline nature is not completely comparable with an angle-integrated measurement as in Ref. 16. Dose *et al.* have attributed these features to the high density of states caused by the split π^* bands at the Q symmetry point.[16] In the band-structure calculations[1,17] these flat π^* bands at Q are located at 1.7 and 2.2 eV, which would match the broad shoulder in Fig. 1(a), but not the G feature at 1.8 eV higher energies. It is now interesting to compare this result for polycrystalline graphite with an inverse-photoemission spectrum of HOPG. Two such examples are shown in Figs. 1(b) and 1(c), with a difference at $E_F+2.5$ eV (arrow) owing to different typical cleavages of the HOPG. We were not able to deliberately prepare one or the other surface when we were peeling HOPG *in situ*, but we believe that curve (b) corresponds to the "best" surface, since exposure of such a surface to activated oxygen (O_2^*) or hydrogen (H_2^*) resulted in an inverse-photoemission spectrum [curve (d)] which resembled that of curve (c), i.e., a quenching of some spectral intensity around 2.5 eV (arrow) occurred. This may also be interpreted as an increase of intensity around 1.7 eV. At this energy the π^* bands are located at Q, but not at Γ, so that a strong $k_{\parallel}$ broadening would be required to explain the 1.7-eV feature in the normal-incidence ($k_{\parallel}=0$) spectra of Figs. 1(c) and 1(d). Structure at 1.7 eV is also discernible in the data of Fauster *et al.*,[4] although the authors did not specifically discuss it. With increasing primary energy, its intensity diminishes indicating a low-angular-momentum character, i.e., s-like character, which disqualifies an interpretation as being due to π^* bands together with a strong $k_{\parallel}$ broadening. We therefore prefer to call attention to the spectral intensity around 2.5 eV, which exhibits a strong surface sensitivity, either owing to "bad cleavages" or exposure to O_2^* and/or H_2^*. Exposure of a "well-cleaved" surface as in Fig. 1(b) to nonactivated H_2 or O_2 did not affect the spectra at all. Hence, the appearance of a structure around 1.7 eV in Figs. 1(c) and 1(d) seems to be caused by the quenching of a rather broad (≈1.5 eV) surface-sensitive feature located at $E_F+2.5$ eV, although some indirect transitions must occur in order to produce the spectral intensity around 1.7 eV. We believe that this surface sensitivity is due to extrinsic surface states, i.e., defects, steps, grain boundaries, disordered clusters, etc., and not to intrinsic surface states split-off from the interlayer band as predicted by Posternak *et al.*[5] to occur at $E_F+3.6$ eV. Since it is known[18] that HOPG is atomically flat on a $(100\ \text{Å})^2$ scale, i.e., it has a rather low surface-step density, local defects are presumably the reason for the extrinsic surface states around 2.5 eV. This will be discussed in more detail below in conjunction with the tunneling spectra.

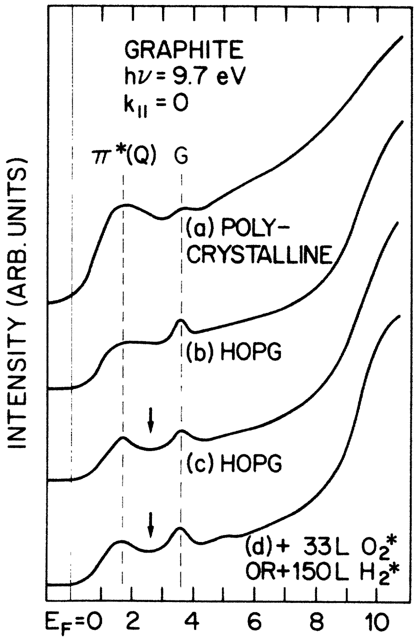

FIG. 1. Normal-incidence inverse-photoemission spectra at $h\nu=9.7$ eV of (a) polycrystalline graphite, (b) peeled HOPG, (c) peeled HOPG (different surface), and (d) plus activated hydrogen or oxygen. The dashed lines denote the positions of the π^* band at the Q point at 1.7 eV (from Ref. 1) and the surface state denoted G as predicted in Ref. 5. The arrow stresses the region around 2.5 eV, which is dependent on surface preparation [curve (b) vs (c)] or can be quenched by activated gasses [curve (b) vs (d)].

The assignment by Posternak *et al.*[15] of the 3.6-eV feature in the inverse-photoemission data of Fauster *et al.*[4] to an intrinsic surface state actually motivated the gas-exposure experiments presented in Fig. 1. As in Ref.

4, we do observe a pronounced peak at $E_F + 3.5$ eV denoted G in our normal-incidence spectra of HOPG [cf. Fig. 1(b)]. However, this feature is not affected by exposure to activated hydrogen and/or oxygen [see Fig. 1(d)] or surface imperfections [see Fig. 1(c)], as this was observed for surface states on Ag(110),[8] Ag(100),[9] Cu(110),[10] and Au(110),[11] employing inverse photoemission; and small amounts of water which adsorb on HOPG at 110 K as monitored by ultraviolet photoemission (not shown) do not quench the 3.5-eV feature in contrast to H_2O on Ag(100).[9] Of course, one could argue that the various gases do not stick to the rather inert HOPG, leaving the 3.5-eV peak unaffected. Since changes occurred around 2.5 eV [cf. Figs. 1(b) and 1(d)], and a change of the work function was monitored by ultraviolet photoemission spectroscopy as the secondary-electron cutoff, we can exclude a zero-sticking coefficient for water and activated H_2 and O_2 on HOPG. In comparison, Au(110) is also expected to be very inert, but its surface states could indeed be quenched by activated oxygen.[11]

The surface state predicted by Posternak *et al.*[5] is split-down by 0.3 eV from the three-dimensional interlayer band, and extends about three layers into the bulk,[5] which is about the same distance as calculated[19] for the intrinsic surface states on the noble-metal surfaces that are also *s*,*p*-like. A similar behavior with gas exposure should therefore be expected. Hence, we conclude that the feature at $E_F + 3.5$ eV in Fig. 1 cannot be related to any surface-state band, in contrast to the calculations of Posternak *et al.*[5] We therefore prefer an interpretation of the 3.5-eV peak in terms of bulk states, e.g., possibly being due to nondirect transitions into the high density of states at the bottom of the interlayer band as discussed by Fauster *et al.*[4] This is corroborated by the fact that even in Fig. 1(a) a weaker structure still exists at 3.5 eV in the case of polycrystalline graphite. Its intensity is attenuated by a factor of ≈ 3 as compared to HOPG [Fig. 1(b)] owing to the nonconservation of **k**. As an illustration, in Fig. 2 we show ultraviolet photoemission data taken at $h\nu = 21.2$ eV (He I) of polycrystalline [curve (a)] and highly oriented graphite [curve (b)]. The well-known[20,21] secondary-electron peak 2.8 eV above the vacuum-level cutoff, which corresponds to σ bands at $E_F + 7.5$ eV, is clearly visible in both spectra shown in Figs. 2(a) and 2(b), but is also attenuated by a factor of ≈ 5 relative to the secondary-electron background in polycrystalline graphite. In summary, the inverse-photoemission peak at $E_F + 3.5$ eV is present in polycrystalline graphite as well as HOPG, and cannot be quenched by activated gases or water adsorption at 110 K. All this suggests bulk electronic states as its origin.

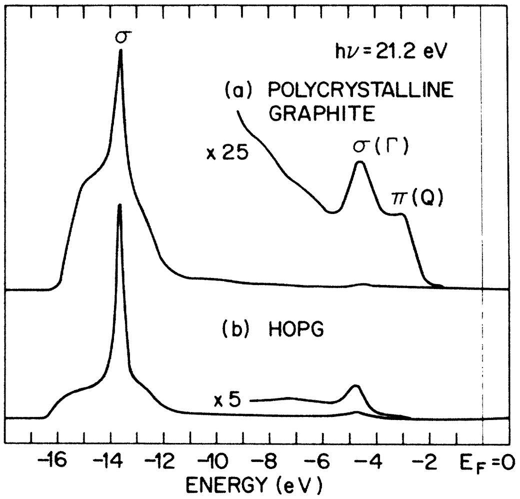

FIG. 2. Ultraviolet photoemission at $h\nu = 21.2$ eV (He I) of polycrystalline [curve (a)] and highly ordered [curve (b)] graphite. The valence-band features at -3 and -4.5 eV correspond to flat π and σ bands, respectively (see Ref. 21). The secondary-electron feature 2.8 eV above the cutoff is due to unoccupied flat σ bands (cf. Ref. 20) and is much less pronounced (factor of 3) in polycrystalline graphite. The work function for HOPG as determined from the cutoff is $\Phi = (4.7 \pm 0.1)$ eV, in agreement with Ref. 20.

In the following we discuss the tunneling data obtained from HOPG and compare it with the inverse-photoemission results. In Fig. 3 the tunneling spectrum (dI/dV versus V) of HOPG is presented for a voltage range of 4 V. Three features are observed, and their inflection points are marked by tick marks at 1.7, 2.5, and 3.3 V. Since we only expect bulk states or intrinsic surface states to contribute to the tunnel current,[7] no Stark shift of the electronic levels by the external field of the tip has to be taken into account. This is in contrast to image-potential surface states which extend more into the vacuum.[11] Therefore, we may compare the spectrum of Fig. 3 directly with ground-state calculations[7] as well as with inverse-photoemission data, which, for the image states as well, represent the field-zero case.[11] A difference between tunneling and inverse-photoemission spectros-

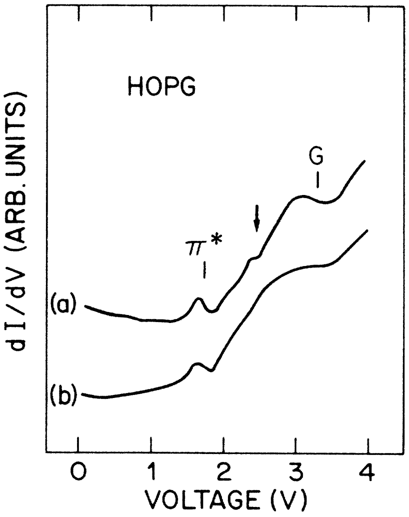

FIG. 3. Tunneling spectra of HOPG: (a) and (b) different spots on same or different surfaces. The feature at 1.7 eV corresponds to bulk π^* bands, the structure around 2.5 eV (arrow) is associated with extrinsic surface states [compare curves (a) and (b)], and the bottom of the interlayer band produces the broad feature around 3.3 eV.

copy concerns the $k_{\parallel}$ resolution. While the inverse-photoemission spectra of Fig. 1 were taken in normal incidence, i.e., $k_{\parallel}=0$, the tunnel current averages over all $k_{\parallel}$ with some weighting of the $k_{\perp}$ component.[22] Therefore, in Fig. 3 we may associate the structure at 1.7 V with the unoccupied π^* bands at the Q point, which should not be observed if $k_{\parallel}=0$ were strictly fulfilled in tunneling spectroscopy. The weaker feature at 2.5 eV was sometimes observed and sometimes not [cf. Figs. 3(a) and 3(b)]. Even on the same surface, it was found at some places and not at others. This finding corroborates the inverse-photoemission result discussed above, namely some surface-sensitive electronic states must exist which are confined to the tunneling area of several hundred Å^2 as determined from I-versus-s measurements. We can therefore exclude steps and grain boundaries as origins for the extrinsic surface states around 2.5 eV, but carbon adatoms, defects, or carbon clusters could account for them.

Around 3.3 V we note a broader feature in the tunneling spectrum which we associate with the 3.5-eV peak of the inverse-photoemission curves in Fig. 1, for which we have excluded an intrinsic surface-state character (see above). On a first inspection this seems to agree with the calculated[7] (dI/dV)-versus-V curve for graphite, which exhibits the inflection points for the π^* bands at 1.7 V and for the intrinsic surface state of Posternak *et al.* at ≈ 3.5 V. However, their relative intensity ratio is calculated[7] to be 10, while we obtain a factor of 4 more or less independent of the tip-surface distance $s \lesssim 5$ Å. Since the calculation[7] of the tunneling spectrum made use of the surface-electronic structure of Posternak *et al.*,[5] which had yielded the intrinsic surface state, an increase in s was calculated to produce an enhanced surface sensitivity which resulted in a relative increase of the surface-state feature in the tunneling spectrum in contrast to our experimental observation (not shown). We take this as another indication that the bulk interlayer band and the high density of unoccupied states associated with the bottom of this band are responsible for the tunneling feature at 3.3 V, as this was also concluded from the inverse-photoemission results (see the discussion above).

In summary, we have applied inverse-photoemission and tunneling spectroscopy to the basal plane of graphite and find very good agreement for unoccupied bulk and surface electronic states with respect to their energetic positions. The π^* band produces a feature at $E_F + 1.7$ eV; extrinsic surface states which can be quenched by activated gases or water exist around $E_F + 2.5$ eV, and the bottom of the bulk interlayer band is found at 3.5 eV. There is no evidence for an intrinsic surface-state split-off from the interlayer band.

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[1] N. A. W. Holzwarth, S. G. Louie, and S. Rabii, Phys. Rev. B **26**, 5382 (1982).

[2] M. Posternak, A. Baldereschi, A. J. Freeman, E. Wimmer, and M. Weinert, Phys. Rev. Lett. **50**, 761 (1983).

[3] C. F. Hague, G. Indlekofer, U. M. Gubler, P. Oelhafen, H. J. Güntherodt, and J. Schmidt-May, Solid State Commun. **48**, 1 (1983).

[4] T. Fauster, F. J. Himpsel, J. E. Fischer, and E. W. Plummer, Phys. Rev. Lett. **51**, 430 (1983).

[5] M. Posternak, A. Baldereschi, A. J. Freeman, and E. Wimmer, Phys. Rev. Lett. **52**, 863 (1984).

[6] N. A. W. Holzwarth, S. G. Louie, and S. Rabii, Phys. Rev. B **30**, 2219 (1984).

[7] A. Selloni, P. Carnevalli, E. Tosatti, and C. D. Chen, Phys. Rev. B 31, 2602 (1985).

[8] B. Reihl, R. R. Schlittler, and H. Neff, Phys. Rev. Lett. **52**, 1826 (1984).

[9] B. Reihl, K. H. Frank, and R. R. Schlittler, Phys. Rev. B **30**, 7328 (1984).

[10] B. Reihl and K. H. Frank, Phys. Rev. B 31, 8282 (1985).

[11] G. Binnig, K. H. Frank, H. Fuchs, N. Garcia, B. Reihl, H. Rohrer, F. Salvan, and A. R. Williams, Phys. Rev. Lett. **55**, 991 (1985).

[12] P. W. Erdman and E. C. Zipf, Rev. Sci. Instrum. **53**, 225 (1982).

[13] V. Dose, Appl. Phys. **14**, 117 (1977); B. Reihl and R. R. Schlittler, Phys. Rev. B **29**, 2267 (1984).

[14] J. K. Gimzewski, A. Humbert, J. G. Bednorz, and B. Reihl, Phys. Rev. Lett. **55**, 951 (1985).

[15] J. W. Gadzuk and E. W. Plummer, Rev. Mod. Phys. **45**, 487 (1973).

[16] V. Dose, G. Reusing, and H. Scheidt, Phys. Rev. B **26**, 984 (1982).

[17] R. C. Tatar and S. Rabii, Phys. Rev. B **25**, 4126 (1982).

[18] R. Miranda, N. Garcia, A. M. Baro, R. Garcia, J. L. Pena, and H. Rohrer, Appl. Phys. Lett. **47**, 367 (1985).

[19] K. M. Ho, B. N. Harmon, and S. H. Liu, Phys. Rev. Lett. **44**, 1531 (1980); K. M. Ho, C. L. Fu, S. H. Liu, D. M. Kolb, and G. Piazza, J. Electroanal. Chem. **150**, 235 (1983).

[20] R. F. Willis, B. Feuerbacher, and B. Fitton, Phys. Rev. B **4**, 2441 (1971).

[21] U. Gubler, J. Krieg, P. Oelhafen, P. Pfluger, H. J. Güntherodt, E. Cartier, and F. Heinrich, in *Physics of Intercalation Compounds,* Vol. 38 of *Springer Series in Solid State Sciences,* edited by L. Pietronero and E. Tosatti (Springer, New York, 1981).

[22] N. D. Lang, Phys. Rev. Lett. **55**, 230 (1985).