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Gap opening in the surface electronic structure of graphite induced by adsorption of alkali atoms: Photoemission experiments and density functional calculations

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The adsorbate-substrate interaction for Na and K on highly oriented pyrolytic graphite (HOPG) has been investigated by photoemission and by density functional calculations. With increasing coverage a peculiar spectral structure develops below the Fermi level reminiscent of the one observed for Cu/Xe/HOPG and formerly interpreted in terms of a Fano resonance. In contrast, we show that this unusual spectral feature reflects a surprising gap opening in the surface electronic structure of graphite owing to charge transfer upon alkali metal adsorption. This finding allows us to put forward a unified picture for the electronic structure changes upon adsorption of alkali metals (Na, K) on HOPG as well as of alkali and alkalilike metals on noble gas spacer layers supported on HOPG.

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The adsorption of alkali metals on solid surfaces is a fascinating research area, as these are model systems for the adsorbate-substrate interaction.[1,2] Here the decisive idea of the formation of electrical double layers for electron transfer from adsorbate to substrate has been pioneered by Langmuir[3] and Gurney.[4]

Of specific fundamental interest is the adsorption of alkali metals on graphite[5–12] with its quasi-two-dimensional electronic and crystallographic structure.[13] The low density of states (DOS) at the Fermi level (E_F) of this semimetal suggests that even a small charge transfer from adsorbate to substrate should noticeably affect its electronic properties.[8] In the limit of low concentration, well-below one monolayer, alkali adatoms form a dispersed phase and transfer charge to graphite.[11] However, it is not clear whether this charge is completely localized on the substrate (ionic state), or if an occupancy of the *s*-derived state is still present (partially ionic state with some covalent character). Recently, the adsorption of Na on graphite has been investigated by density functional theory, indicating a weak interaction and a charge transfer of 0.5 electrons from Na to the substrate.[12] However, the charge transfer determined by different experimental techniques varies considerably. Work function measurements[7] and core-level photoelectron spectroscopy[10] determined the charge transfer to HOPG to be 0.5 electrons and 0.15 electrons per K atom, respectively, indicating a covalent character of the bonding. In contrast, x-ray absorption spectroscopy determines the K bonding on the graphite surface to be mainly ionic, with the 4*s* resonance located above the Fermi level E_F.[9] One solution proposed to explain these discrepancies is the splitting of the K 4*s* level into bonding and antibonding components, due to interaction with the graphite orbitals.[11] This puzzling situation motivated us to scrutinize the crucial assumption made hitherto: is it really justified to describe the interaction solely within the rigid-band model, i.e., to neglect, apart from band filling, any modification of the substrate DOS?

Here we present the results of photoemission experiments performed on prototypical simple adsorption systems, Na and K on graphite, for coverages below 0.1 monolayer (ML), where 1 ML is defined as one alkali atom per graphite unit cell. Together with density functional (DFT) calculations we show that alkali adatoms are not only responsible for a charge transfer inducing a sensible work function decrease, but that they are also at the origin of a surprising modification of the graphite surface electronic structure: the opening of a band gap in the occupied part of the DOS.

The experiments were performed in an ultrahigh vacuum chamber equipped for ultra-violet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS). A high intensity gas discharge lamp (Gammadata) combined with a homebuilt monochromator allows us to measure satellite-free spectra excited by the main resonance line He I (21.2 eV). The photoemitted electrons are collected by a hemispherical analyzer (HA 150 from VSW), with angular resolution of ±2°, and total instrumental energy resolution set to 50 meV. The work function was determined by applying a negative voltage to the sample and by measuring the secondary electron onset. The HOPG substrate, freshly cleaved, was mounted on a cold-finger held at $T=50$ K by a closed cycle He refrigerator. The temperature was measured by means of a thermocouple fixed on the sample holder. A retractable electron gun allows rapid heating of the sample up to 1200 K for the cleaning procedure. Na and K were evaporated from directly heated dispensers (Saes Getters) on the substrate held at 50 K. The alkali coverage was determined by XPS.

The semimetallic character of graphite originates from the valence and conduction π bands meeting and slightly crossing at E_F along the K-H line of the 3D Brillouin zone (at the K point in a simplified 2D model, shown in Fig. 1).[13,15] Thus, the expected band filling due to charge transfer will be particularly evident by probing this high-symmetry point of the Brillouin zone.[6] Figure 1(a) shows an UP spectrum acquired on bare HOPG, at an emission angle of 54° with respect to normal emission, corresponding to the K point at E_F for He I photon energy. The emission intensity decreases approaching

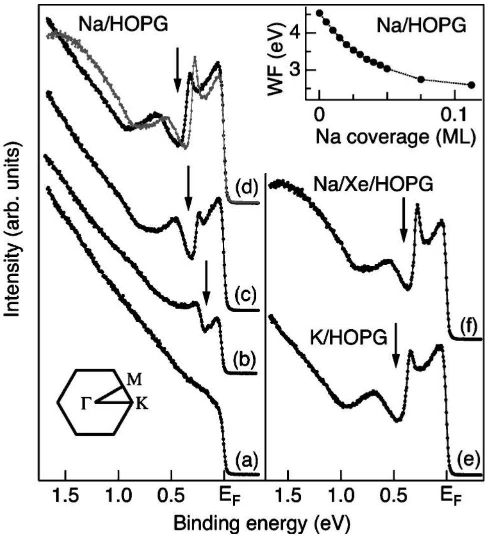

FIG. 1. UP spectra (He I) measured on HOPG (a) and for increasing Na concentration, (b) 0.01 ML, (c) 0.02 ML, (d) 0.04 ML, [grey line: Na/Xe/HOPG, same as (f)]; (e) measured on 0.04 ML of K on HOPG. Spectra (a)–(e) were measured at an emission angle of 54° with respect to normal emission. (f) Na/Xe/HOPG, for Na coverage of 0.04 ML (normal emission geometry). Inset: work function (WF) change vs Na coverage on HOPG. The 2D graphite Brillouin zone is also sketched.

E_F, where a finite spectral weight is observed, which hints to the existence of a tiny Fermi surface.[14–16] Figure 1(b)–1(d) shows coverage-dependent UP spectra obtained in the same geometry from Na on HOPG. The spectra display an intriguing resonance-shaped emission close to E_F, superimposed on a V-shaped background (including the former empty states, see Fig. 3), the minimum of which shifts towards higher binding energies with increasing Na coverage. For K on HOPG [spectrum (e)] a very similar spectral shape as in (d) is found. Here, however, we focus our investigation on Na owing to the well-known intercalation tendency of K,[7,17] an effect which we also observe after heating the sample with the consequence that the peculiar spectral structure vanishes. The V-shaped background in the spectra nicely reflects the expected filling of the graphite π*-band due to charge transfer from the alkali adatom to the substrate.[6,12]

Interestingly, the resonancelike feature observed in the spectra (b)–(e) shifts from 0.2 eV at 0.01 ML of Na (b) to 0.4 eV at 0.04 ML (d), and shows a simultaneous broadening. The inset in Fig. 1 displays the measured work function decrease with increasing Na coverage (below 0.1 ML) on HOPG. For a coverage of 0.04 ML of Na [spectrum (d)] the work function amounts to 3.21 eV, indicating a lowering of about 1.3 eV with respect to bare HOPG. This behavior is expected for a dispersed phase of alkali adatoms.[11] Indeed, scanning tunneling microscopy measurements performed on Na/HOPG confirm that the adatoms are adsorbed in a dispersed phase, forming very small aggregates of few atoms per cluster and affecting the work function via charge transfer and/or polarization.[2,7,11,12]

These findings corroborate the hypothesis that the main requirement for the observation of the resonancelike emission in the spectra is a lowering of the work function, induced by charge transfer from adsorbate to substrate. This spectral structure is reminiscent of the one found for Cu/Xe/HOPG (Refs. 18,19) and which we observe also for Na/Xe/HOPG [Fig. 1(f), and, for comparison, superimposed (grey) to (d)]. Here the nonzero DOS at E_F in normal emission geometry originates from the π-band at the K point which is folded into the Γ point by the commensurate Xe layer.[18] As in the present case of Na/Xe/HOPG, Na/HOPG, and K/HOPG, the appearance of this resonance-shaped structure in the photoemission spectra of Cu/Xe/HOPG was also related to a lowering of the work function due to charge transfer from adsorbate to substrate.[20] For Cu/Xe/HOPG the spectral feature has been interpreted in terms of a Fano interference effect between a discrete atomic level and a continuum of states.[18] The key idea in this interpretation was that the Cu 4*s* level is resonant with the occupied DOS of the system. However, the coverage-dependent work function decrease of 0.6 and 1.3 eV, measured subsequently for Cu/Xe/HOPG (Ref. 20) and Na/HOPG, respectively, reflects the depopulation of the outer metal *s* state leading to an essentially ionized Cu 4*s* and Na 3*s* level, respectively, in resonance with the unoccupied DOS. Consequently, empty state spectroscopies, e.g., inverse photoemission, are expected to display a Fano resonance in the excitation spectra of these systems but for the occupied states this interpretation has to be dismissed.

The origin of this unusual spectral feature is linked to the peculiar band structure of graphite. At a Brillouin zone boundary the conventional situation is that the two wave functions corresponding to conduction and valence bands pile up electrons at different locations with respect to the atoms and thus experience a different mean potential—the origin of a gap.[21] On the contrary, precisely at the K-point in graphene (one two-dimensional graphite sheet), and along the K-H line in graphite, this difference in the potential vanishes because of the symmetry of the graphite lattice. The matrix element between the conduction band and the valence band vanishes (no hybridization), giving rise to the direct zero gap at the K point, which is the origin of the semimetallic character of graphite.

Upon adsorption the Na atom transfers a fraction of an electron into the substrate. The band filling shifts the Fermi energy above the energy of the DOS minimum of pure graphite. In addition, the weak interlayer coupling modifies the charge transfers. Consequently, the energy position of the DOS minimum for each graphene layer is displaced in going from a surface to a subsurface layer. Now the symmetry of the graphite lattice is perturbed and the zero gap at the K point (see Fig. 2 for a graphene sheet) is expected to open "naturally" owing to hybridization-induced noncrossing of bands. This effect is related to band bending in semiconductors where tens to hundreds of atomic layers are affected by the Fermi level adjustment. Here only a few surface layers are involved in the charge transfer and for a system with many layers only a dip in the DOS near the surface would remain.

DMOL^3 density functional calculations[22] of the band structure for Na on graphite confirm this reasoning. A series of graphite slab supercells was studied, starting from monolayer

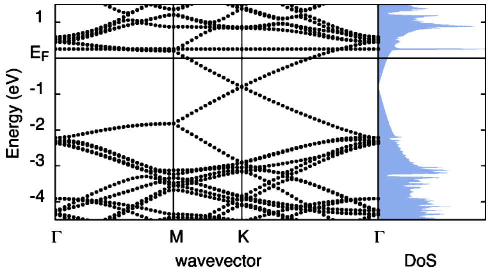

FIG. 2. (Color online) Band structure and DOS of a 5×5 graphene supercell with one adsorbed Na atom. The Na 3*s* induced level is the flat feature visible at 0.2 eV above E_F.

graphene to six layer 3×3 graphene unit cells with one adsorbed Na (corresponding to a coverage of 0.11 ML Na) and up to five layer 5×5 with one adsorbed Na (corresponding to 0.04 ML Na) supercells.[24] It is found that Na resides 0.232 nm above the surface. A calculation for one single layer graphite with adsorbed Na yields the V-shaped DOS known from graphene with the Fermi energy shifted a fraction of an eV into the former conduction band, because of band filling due to the charge transfer from the adsorbed Na (Fig. 2). For two layers with an adsorbate a small gap arises at the former DOS minimum. The sum rule for the states in k space results in a peaked DOS on both sides of the gap.[25] For models with more than two layers the gap in the occupied DOS remains and more features appear. Figures 3(a) and 3(b) show the total DOS for bulk graphite and for a three layer 5×5 model with adsorbed Na, respectively.[26] The two DOS are aligned to clearly show the band filling due to charge transfer from the Na atom to the substrate. In (b) a gap of width $\Delta \approx 0.15$ eV is observed in the occupied DOS at about -0.4 eV displaying an enhanced DOS at the gap edges. The Na 3*s* resonance is located 0.5 eV above E_F, indicating an essentially ionized Na adatom. The transferred electron stays in the first graphite layer, corresponding to 0.02 el/C atom in the case of a 5×5 model.

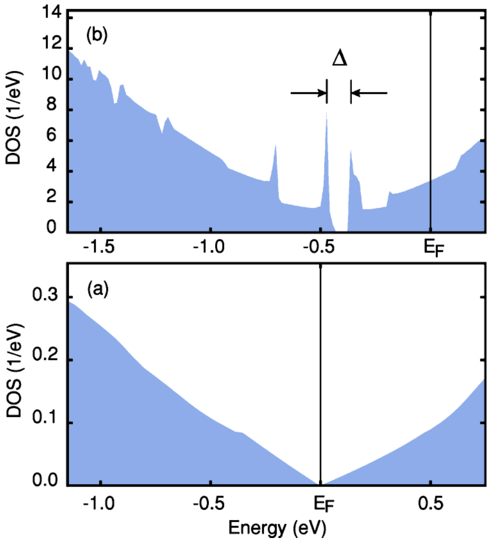

FIG. 3. Calculated DOS for (a) bulk graphite and (b) a three layer 5×5 model with one adsorbed Na atom (0.04 ML coverage). Note the opening of a gap of width $\Delta \approx 0.15$ eV around -0.4 eV.

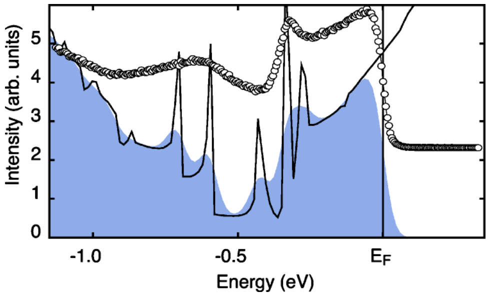

FIG. 4. Comparison between calculated DOS and measurement. Black line: five layer 5×5 model, DOS of the surface sheet counted twice and subsurface once; filled curve: same DOS, broadened by a Gaussian. White circles: spectrum (d) of Fig. 1, vertically shifted for clarity.

For a surface layer in equilibrium with bulk graphite the two Fermi levels must align and the space charge leads to band bending near the surface with the adsorbate. This situation is similar to the one for materials supporting surface states and is also closely related to the origin of surface core-level shifts observed in photoemission.[23]

We emphasize that the gap is not a spurious issue of the adatoms eventually forming a perfectly regular supercell in the calculation. The calculation for a primitive cell of a two layer graphite slab under an applied external field shows that this charge redistribution between the layers is already sufficient to open the gap. Subsequently, by maintaining the field and charging the graphite slightly (0.05 el/4 atoms) the Fermi energy is shifted into the conduction band (the counter charge is uniformly spread out, the main part falls into the interstitial.) This calculation is also able to model the experimentally observed Na-adatom concentration-dependent shift of the gap towards higher binding energies, as well as a concomitant increase of the gap width.

Figure 4 shows a direct comparison between calculation and measurement. The DOS of a five layer 5×5 model (black line), in which the surface sheet is counted twice and the subsurface once, is displayed together with the same DOS broadened to account for the experimental resolution (Gaussian of 70 meV of FWHM, and thermal contribution of 4 meV) (filled curve). The latter should be compared with spectrum (d) of Fig. 1 (white circles). The comparison between total DOS and angle-resolved spectra is justified, as the DOS close to E_F originates exclusively from contributions from the K point (see Fig. 2). We note, however, that due to the polycrystalline structure of HOPG we average over a ring with the radius Γ-K in the Brillouin zone. Considering the factors which influence the measured spectra (energy and angular resolution, electron mean free path, i.e., the contribution from subsurface layers where the charge transfer induced gap closes and becomes again the zero gap of graphite, matrix-element effects, polarization, final-state effects, and lifetime width[16]), the calculated DOS for Na on graphite presents a striking similarity with the photoemission spectra. Furthermore, based on the model calculation shown in Fig. 3, one can envisage a continuous change from Figs. 3(a) and 3(b), i.e., a shift of the Fermi energy with a concomitant gap opening. Then the comparison with the experimental spectra shown in Fig. 1 for increasing Na coverage is indeed convincing. Evidently, in the case of graphite, the charge transfer and the related band bending have a surprising effect on the DOS. Following conventional wisdom one would expect that the layer DOS is shifted according to the band bending. This would result only in a kink in the DOS. However, the experiment clearly shows a dip flanked by peaks which is an unambiguous manifestation of a surface gap opening.

These results establish a unified picture of the spectroscopic manifestations of the electronic structure changes upon adsorption of alkali atoms (Na, K) on graphite and of alkali and alkalilike metal atoms (Na, Cu) on noble gas spacer layers (Xe, Ar, Kr) supported on graphite. The charge transfer from adsorbate to substrate leads to band filling and to a concomitant shift of the Fermi energy towards higher energy. The minimum in the graphite DOS, the zero gap at E_F, is now found below the Fermi energy and, surprisingly, opens into a surface gap within the occupied DOS, at both sides of which the DOS is enhanced. Owing to the charge transfer the metal s state is essentially ionized and resonant with the *unoccupied* DOS. Consequently, the former interpretation of the resonancelike emission close to E_F in terms of a Fano resonance[18] has to be dismissed and may be valid for spectroscopies probing the *unoccupied* DOS of these systems. The unusual spectral feature reflects the opening of a gap in the *occupied* electronic states of the graphite substrate surface layers.

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[24] The calculations were performed using the Perdew-Wang local density functional PWC. SCF iterations were done using a 12×12 unshifted k mesh resulting in 31 symmetry unique reciprocal space vectors. The final density of states was found with the tetrahedron method based on a 60×60 unshifted mesh resulting in 631 symmetry unique k points.

[25] This is similar to the opening of a superconducting gap where the normal electron states which have been in the gap region pile up at the gap edges in the superconducting state in order to conserve the total number of states.

[26] Bulk graphite: k mesh for tetrahedra $24 \times 24 \times 6$; three layer 5×5 model with adsorbed Na: k mesh for tetrahedra $60 \times 60 \times 1$.