Alkali-metal-deposition-induced energy shifts of a secondary line in photoemission from graphite

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Photoemission spectra from graphite recorded along the surface normal reveal a state 7.6 eV above the Fermi level populated by secondary electrons. We have studied this emission line both for pristine graphite and after deposition of different alkali metals (Na, K, Rb or Cs). Common for all the alkali metals is that initially upon deposition the work function decreases rapidly and then saturates at a submonolayer coverage. In the low coverage range the secondary line splits into two components one of which remains at nearly constant energy. The other shifts to lower energy upon deposition in proportion to the work function change $\Delta E = \alpha \Delta e\Phi$, where α^{-1} is approximately proportional to the radius of the alkali metal atom. Of main interest is the interpretation of two secondary lines which appear as the evaporation is continued beyond saturation of the work function for K, Rb or Cs but not for Na. Based on the common behavior for the three heavier alkali metals we revise an earlier interpretation on results for only Na and K and suggest as an alternative that the secondary doublet is characteristic of an ordered 2×2 atomic layer of alkali metal. The additional emission lines are then due to electrons occupying final states at the midpoints of the boundaries of the hexagonal Brillouin zone and which are diffracted into the normal direction.

I. INTRODUCTION

Energy shifts are a main source of information when photoemission is applied to surface systems. Core level binding energies give information about the existence and number of inequivalent sites. Surface states may survive upon adsorption and have a coverage dependent binding energy.[1] Likewise quantum well like states in an overlayer are observed to shift in energy as more atoms are added to an incomplete outermost atomic layer.[2] For a semiconductor the entire spectrum shifts rigidly as the surface photo-voltage is modified due to illumination[3] or adsorption.[4]

While the observations referred to above concern filled states, photoemission spectra may also show emission lines due to final states populated by secondary electrons. This type of emission has received relatively little attention in the study of surface systems. In this paper we report on a detailed study of a secondary emission peak which is due to a zone center state of σ-character 7.6 eV above the Fermi level, E_F, in graphite and the evolution of this upon deposition of different alkali metals (Na, K, Rb, Cs).

Interesting with the alkali metal/graphite surface systems is a phase transition, first observed for K/graphite,[5] occurring at a submonolayer coverage. For coverages below this threshold the alkali metal atoms form a dispersed phase whereas above it a close-packed metal phase coexists with the dispersed one.[5] For graphite as well as for a metal substrate there is a transfer of electronic charge to the substrate from an adsorbed alkali metal atom. The surface dipoles thus created cause a rapid drop of the work function initially upon deposition. The important difference between graphite and a metal is that graphite is a semimetal with few states near the Fermi level that can accommodate the transferred electrons. As the coverage is increased these electrons must therefore populate states significantly above the Fermi level of graphite. As discussed in detail by Ishida and Palmer[6] this, at some coverage, becomes energetically unfavorable making con-

densation of alkali metal the preferred alternative. As more alkali metal atoms are deposited the area of the condensate increases, eventually covering the entire surface.

II. EXPERIMENT

The photoemission experiments were performed at BL52 in the MAX synchrotron radiation laboratory, Lund Univer-
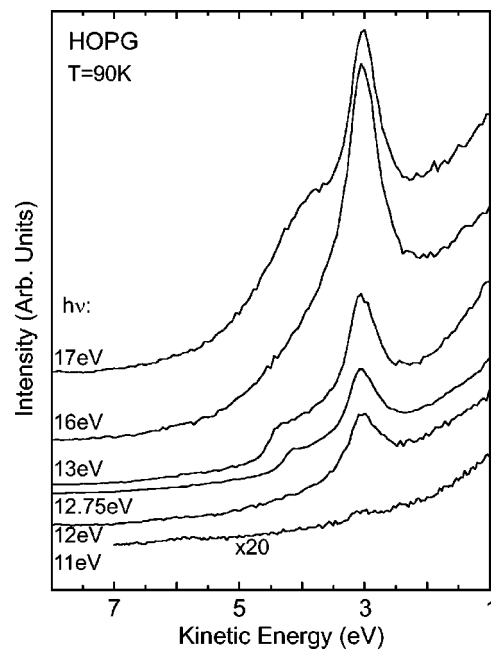

FIG. 1. Photoemission spectra from pristine graphite recorded at different photon energies, $h\nu$, as indicated in the diagram. The peak at 3 eV has a marked onset at a photon energy between 11 and 12 eV. The upper filled σ-state is visible as a sharp edge at 4.25 and 4.5 eV using photon energies of 12.75 and 13 eV.
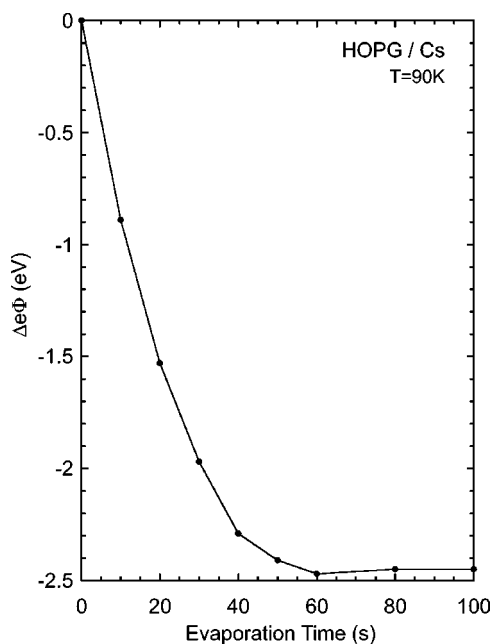
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FIG. 2. Work function change for graphite upon Cs deposition. 1 ML of Cs corresponds to an evaporation time of 350 s.
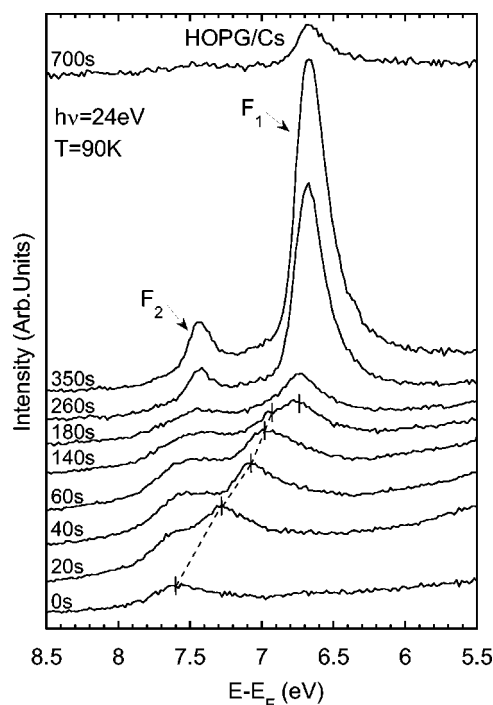
FIG. 3. Photoemission spectra showing the evolution of the final state in graphite upon Cs deposition. The evaporation time for each spectrum is given. At low coverage the state splits and one component shifts to lower energies. At higher coverages ($\geq$140 s) two new final state peaks emerge (labeled F_1 and F_2) at around 6.65 and 7.4 eV above E_F. These peaks grow in intensity until 1 atomic layer of Cs is evaporated, which in this experiment was achieved after 350 s. Upon further evaporation the intensity of these peaks decreases again.

sity, where a normal incidence monochromator provides photons in the energy range from 3.5 to 40 eV. A sample of highly oriented pyrolytic graphite (HOPG) was used as substrate. HOPG consists of microcrystals which have a nearly common *c*-axis but which are azimuthally disordered. The disorder means that in LEED the pattern consists of rings rather than spots. It also means that an off normal photoemission spectrum is integrated over the azimuthal angle. All spectra shown below are recorded along the sample normal. The sample can be cooled to 90 K using LN_2 or 40 K using LHe. The alkali metals are evaporated onto the graphite sample from a heated breakseal ampoule, which is kept at constant temperature typically set to give a monolayer (ML) within 3–10 min. The work function change upon alkali metal deposition is monitored as a shift of the low energy cut-off of the photoemission spectra.

Between experimental runs the sample is cleaned by resistive heating to around 1100 K. This is done by passing a current ($\sim$40 A) through the sample for about 1 min. After heating the low energy cut-off together with the overall appearance of the photoemission spectrum is used to check the cleanliness of the sample.

III. RESULT

A. Pristine graphite

In a photoemission spectrum from graphite recorded along the sample normal there appears a distinct line 3 eV above the low energy cut-off independent of the photon energy used if this exceeds a critical value (Fig. 1). Such behavior is typical for a peak, which is due to a state above E_F. Photoelectrons are scattered into the state giving a peak at fixed kinetic energy. The secondary peak in graphite at 7.6 eV above E_F has been noted in previous experiments[7–11]

and based on energy band calculations it is assigned to a σ state.[12,13]

As seen in Fig. 1 the peak has an onset for a photon energy between 11 and 12 eV. With a work function of 4.6 eV this means that at threshold the initial state has an energy somewhere between 3.4 and 4.4 eV below E_F.

In the spectra recorded with 12.75 and 13 eV photons there is a sharp edge at 4.25 eV and 4.5 eV kinetic energy (Fig. 1). The change in kinetic energy by the same amount as the change in photon energy indicates that this emission is due to an initial state. Converting the kinetic energy into binding energy gives an initial state energy of 3.9 eV below E_F. We interpret the edge as emission from the upper filled σ-state, which at the zone-center is at 4.1 eV below E_F.[14]

B. Alkali metal covered graphite

Upon alkali metal deposition the evolution of the secondary peak at 3 eV kinetic energy (i.e., 7.6 eV above E_F) reveals two separate coverage stages.

Initially upon deposition there is a nearly linear decrease of the work function when this is plotted versus deposition time. This is illustrated in Fig. 2 for the case of Cs where the work function changes, initially rapidly and then less rapidly, by 2.4 eV after 60 s of evaporation when it levels off. In this low coverage regime the secondary peak splits into two com-
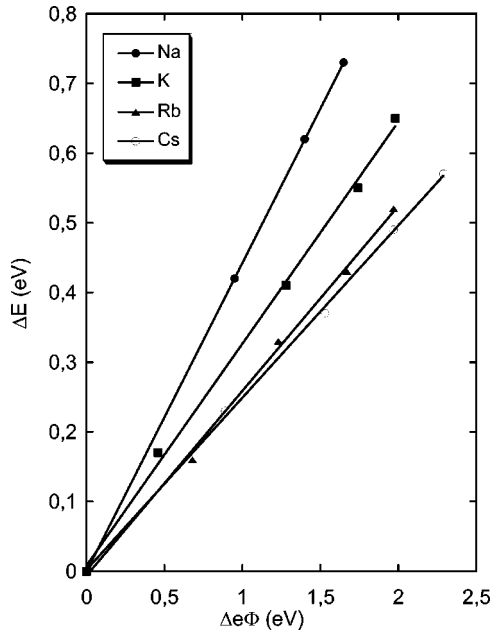
FIG. 4. Energy shift, ΔE, of the shifted component of the final state plotted versus work function change for the four alkali metals studied in this work. The lines drawn are least squares fits to the data points. The slope, α, for the different lines is given in Table I.

ponents one of which shifts toward lower energy while the other remains at approximately constant energy (Fig. 3). A similar split and energy shift occurs for all alkali metals studied in this work, Na, K, Rb and Cs. The energy shift, ΔE, is proportional to the work function change, $\Delta E = \alpha \Delta e \Phi$, but with different constants, α, for the different alkali metals (Fig. 4). The values of α are found to decrease with increasing size of the alkali metal atom and are given in Table I below.

Upon continued deposition beyond saturation of the work function two new peaks emerge (labeled F_1 and F_2 in Fig. 3). Peaks similar to F_1 and F_2 appear also when either K or Rb is deposited (Fig. 5). Noteworthy is that no peaks similar to the F peaks appear when Na is deposited.[15] The very similar coverage dependence of the peak evolution (intensity, energy and width) for K, Rb and Cs suggests that the peaks are due to the substrate although its appearance is induced by alkali metal deposition. After passing a maximum the intensity decays gradually with increasing deposition time as expected for substrate derived peaks.

The new secondary peaks (F_1 and F_2) emerge in concert with emission lines which signals the formation of condensed alkali metal. One characteristic line is the shallow $(n-1)p$ core line which is shifted from the binding energy observed for the disperse phase.[16] Another characteristic emission line is a state S at around 0.5 eV binding energy. The state S is observed only for the three heavier alkali metals having binding energies of 0.57, 0.63, and 0.42 eV for K, Rb, and Cs, respectively. The intensity of peak S and peak F_1 increases upon alkali metal deposition and reaches maximum intensity at the same coverage. As shown for K/graphite in Fig. 6 both peaks then decrease in intensity as more alkali metal is deposited. For a more detailed report on peak S we refer the reader to Ref. 17.
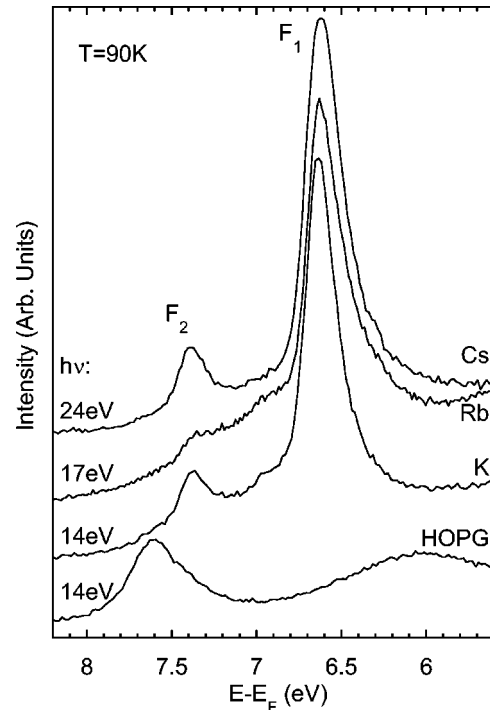

FIG. 5. Photoemission spectra recorded from graphite after deposition of the alkali metal indicated by each spectrum such that peak F_1 has maximum intensity. The energy of F_1 and F_2 is very similar for the three alkali metals.

The intensity of peak F_1 is large compared to all other features in the alkali metal/graphite spectrum and also compared to the final state peak for pristine graphite. This is shown, for the case of Cs/graphite, in Fig. 7 where spectrum A is recorded for pristine graphite and spectrum B for a Cs coverage which gives peak F_1 maximum intensity. The two other strong peaks in this spectrum are due to the spin-orbit split Cs $5p$ level.

For Cs/graphite the evolution of the spectrum upon deposition was monitored at different photon energies. One result of interest is that the strong increase of the peak intensity with increasing coverage observed for peak F is similar above and below the threshold for exciting Cs $5p$ electrons to kinetic energies high enough that the electrons can contribute to F after being inelastically scattered.

IV. DISCUSSION

A. Pristine graphite

The marked onset of the secondary peak for a photon energy between 11 and 12 eV (Fig. 1) indicates that electrons

TABLE I. The proportional constant, α, in $\Delta E = \alpha \Delta e \Phi$ and the calculated distance, d_{cc}, between the center of the alkali metal and the center of the topmost graphene layer are given for the various alkali metals, AM, studied.

AM	Na	K	Rb	Cs
α	0.44	0.32	0.27	0.25
d_{cc}(Å)	2.11	2.61	2.79	3.01

from the upper filled σ-state, 4.1 eV below E_F at the zone center,[14] end up in the final state, 7.6 eV above E_F.

Using 12.75 eV and 13 eV photons one finds a sharp edge (Fig. 1) at a kinetic energy where electrons from the upper filled σ-state are expected. In a previous work on single crystalline films of graphite the upper σ-state was observed as an edge also at photon energies above around 20 eV. The edge developed into a narrow peak when the photon energy exceeded 36 eV. In a plane wave approximation of the final state for a graphene sheet the upper filled σ-state gives no emission in normal direction.[18] It was therefore suggested that the upper σ-line appears in normal emission as a result of diffraction.[14]

The full width at half maximum of around 0.5 eV for the final state peak is small, considering the high energy, 7.6 eV, above E_F. The quasi-particle lifetimes in graphite are however unusual and not inversely proportional to the excitation energy squared as predicted by Fermi liquid theory. Experimental two-photon-photoemission experiments by Xu *et al.* implied a lifetime in the region 0.4–2 eV above E_F which is inversely proportional to the excitation energy.[19] In similar experiments Moos *et al.* did not find any simple power law for the lifetime in graphite.[20] Support for the result obtained by Moos *et al.* is given in calculations by Spataru *et al.*[21] and the deviation from Fermi liquid theory is ascribed to the particular band structure of graphite.

B. Alkali metal covered graphite: Dispersed phase

At low coverage there is a charge transfer from the adsorbed alkali metal atoms to the graphite and hence a lowering of the work function. The partly ionized alkali metal atoms repel each other and are uniformly distributed across the surface, as observed by electron diffraction for K, Rb and Cs on graphite.[5,22,23] In this coverage regime the final state peak splits into two components one of which shifts toward lower kinetic energy as more alkali metal is deposited.

The split is ascribed to a surface-bulk split. The final state is of σ-character and is localized to individual graphene layers thereby reflecting the environment in each graphene layer. The detection of two components, one which remains at nearly constant energy, suggests that the transferred charge mainly resides in the topmost graphite layer.

In a previous study[15] the work function change for the graphite/alkali metal system was regarded as the sum of two contributions, the downshift ΔE of the energy bands in the top graphite layer and the potential difference between the top graphite layer and the alkali metal atoms. This leads to the following expression for the work function change:

$$\Delta e\Phi = \Delta E + \frac{edq}{\epsilon_0 A}, \tag{1}$$

where d is the effective length of the surface dipole, q the transferred charge and A the surface area.

Combining Eq. (1) with the experimental observation $\Delta E = \alpha \Delta e\Phi$ gives
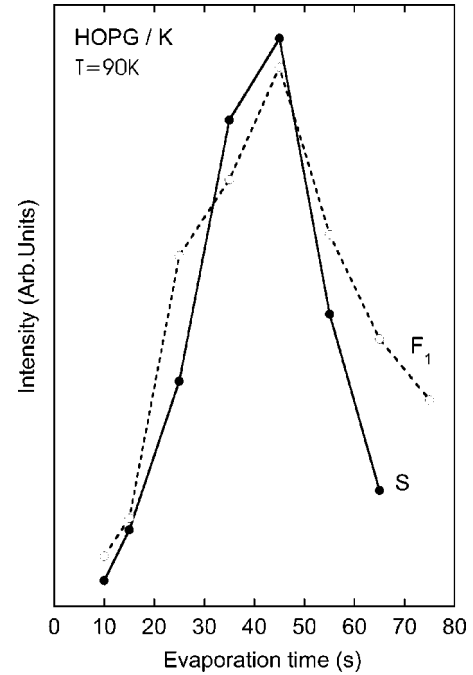

FIG. 6. Intensity of the photoemission peaks due to the new final state peak (corresponding to F_1 in Fig. 3) and a state S, at 0.57 eV binding energy, in the K/graphite system plotted versus potassium deposition time. Both peaks are at maximum intensity after a deposition time of 45 s when a full atomic layer of potassium is obtained.

$$\frac{1}{\alpha} = \frac{q}{\Delta E}\frac{ed}{\epsilon_0 A} + 1. \tag{2}$$

From this one expects decreasing values of α with increasing size of the alkali metal atom. This is based on the reasonable assumption that the same amount of transferred charge, q, to the graphite gives the same energy shift, ΔE, independent of the particular alkali metal responsible for the charge transfer. This means that the fraction $q/\Delta E$ does not depend on the particular adsorbate. It then follows that when d becomes larger α is expected to become smaller.

Furthermore, according to Eq. (2), if $1/\alpha$ is plotted against d for the various alkali metals the data points are expected to fall along a straight line. As a first approximation the length of the surface dipole is taken to be the distance between the alkali metal atoms and the center of the outermost graphene layer, d_{cc}. In the literature one finds only few determinations of d_{cc}. For a 2×2 Cs overlayer on graphite a LEED analysis by Hu *et al.* gives a distance of 2.8 Å.[24] This value differs significantly from the value 3.4 Å, which is obtained from density functional theory (DFT) applied to the same system.[22] DFT calculations by Lamoen *et al.* for the 4×4 and 2×2 K overlayers on graphite[25] yield d_{cc} values near 2.8 Å in both cases.

In the absence of a complete set of reliable values for the alkali metal-graphite distance we choose to calculate d_{cc} using a simple hard sphere model. The atoms are treated as hard spheres making contact with their nearest neighbors and the alkali metal atom is placed above the center of the graph-
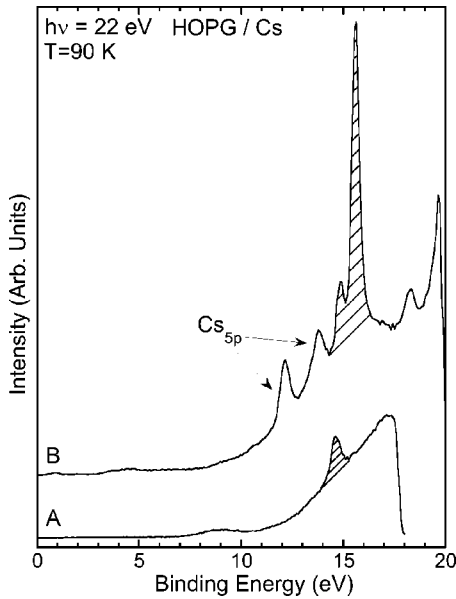
FIG. 7. Photoemission spectra recorded from pristine graphite, A, and after evaporation of 1 ML of Cs, B. The secondary peaks due to the final states and discussed in the text are shaded in the spectra. The shift of the low energy cut-off by around 2.3 eV between the two spectra reflects the reduction of work function upon Cs deposition. The peak at around 18.2 eV binding energy in spectrum B is due to a graphite final state located close to the vacuum level in pristine graphite and thus observed only after a work function reduction.
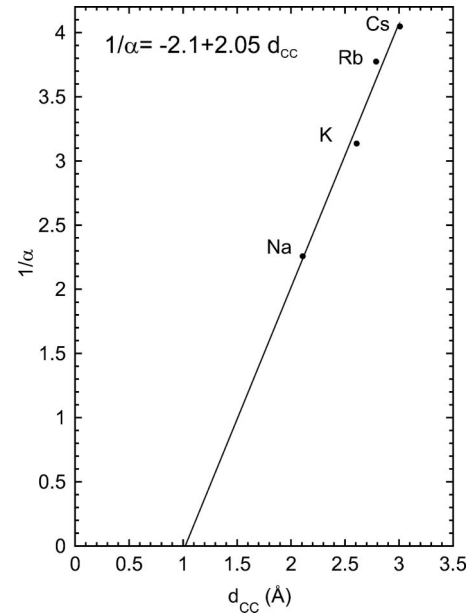

FIG. 8. Plot of $1/\alpha$ versus the distance d_{cc} for the different alkali metals studied in this work. The particular alkali metal is given by each point. The least squares fit equation is given.

ite hexagon. This is the preferred site for both K and Cs.[24,25] The radius of the alkali metal atom is taken to be half the nearest neighbor distance in the bulk metal, obtained from Ref. 26, and the carbon atom radius is chosen to be half the interatomic distance in a graphene layer. The distances d_{cc} obtained in this way are given in Table I.

In Fig. 8 $1/\alpha$ is plotted against d_{cc} and a straight line has been fitted to the data points. From Eq. (2) we expect $1/\alpha=1$ for $d=0$. From the plot one finds that $1/\alpha=1$ at 1.5 Å, which suggests that the dipole length is about 1.5 Å shorter than the center to center distance between the adlayer and the uppermost graphene layer. We note that in the DFT calculation for K/graphite by Lamoen et al.[25] it is found that the charge transferred from the potassium toward the graphite resides between the center of the outermost graphene layer and the alkali metal layer. The distance of the electronic charge to the graphite layer is however appreciably smaller in the calculation, around 0.9 Å, than obtained here. A similar reduction of the effective dipole length was also obtained in a DFT calculation on a $KC_{24}H_{12}$ cluster[27] where the effective dipole length was around 0.7 Å shorter than the center to center distance (2.8 Å).

From the plot in Fig. 8 one can also obtain a rough estimate of the density of electron states in the vicinity of the Fermi level, $n(E_F)$. The slope of the straight line combined with a charge transfer $q=en(E_F)\Delta E$ gives $n(E_F)=0.03$ electron states/eV atom. An assumption then made is that the shift ΔE observed for the final state is the same as the shift of states near E_F. While the value estimated for $n(E_F)$ is much

smaller than typical of a metal it is an order of magnitude larger than the values obtained from energy band calculations. Ahuja et al. obtain 0.0033 electron states/eV atom[28] and Tatar et al. obtain 0.00012 electron states/eV atom.[13]

Values of $n(E_F)$ obtained from specific heat measurements range from 0.006 to 0.013 electron states/eV atom depending on the type of graphite sample used in the experiments.[29] In a later specific heat measurement on HOPG a value of 0.007 electron states/eV atom was obtained.[30] It should be pointed out that in our case we get the DOS for a surface graphene layer perturbed by alkali metal and this may certainly differ from the bulk DOS in graphite obtained from the specific heat measurements. Also, the value we obtain for $n(E_F)$ depends on the values used for the radius of the alkali metal atom. For example, using the radius of the alkali metal ion, obtained from Ref. 26, to calculate d_{cc} a value of 0.024 electron states/eV atom is obtained.

The observation of a proportionality between ΔE and $\Delta e\Phi$ indicates that a rigid downshift of the graphite bands in the vicinity of E_F, to make room for the transferred electrons, might not be an adequate way to describe the electronic structure in the surface region. In the rigid band model, which is often used to discuss charge transfer for alkali metal/graphite systems, the dispersion of the graphite energy bands is assumed to be unperturbed by the presence of the alkali metal and the charge transferred to the substrate is only manifested by a rigid downshift relative E_F of the graphite bands. If this model is applied to the present alkali metal/graphite systems the linear relation between ΔE and $\Delta e\Phi$ implies a constant DOS above E_F.[15] This is in conflict with the nearly linear increase of the DOS near above the deep minimum at E_F obtained in band energy calculations for graphite.[13,28] Possible reasons for the discrepancy are discussed in a previous paper.[15]

C. Alkali metal covered graphite: Condensed phase

Striking with peak F, aside from the high intensity, is that it is observed for K, Rb and Cs but not for Na. Regarding structure Na, like the heavier alkali metals, shows an onset of condensation at a coverage threshold in the monolayer range.[15,31] Merely condensation is thus not sufficient for F to appear. Based on our previous results, which were limited to Na and K, we suggested that the initially formed condensate is an intercalated monolayer for K[17] but an adsorbed one for Na.[15] In earlier reports the K condensate had been assigned to an adsorbed monolayer.[5,6,16] The present observations do not resolve this matter, which is of continuing interest to us.

An alternative interpretation is however suggested by the fact that K, Rb and Cs all form 2×2 ordered layers for the surface systems[31] as well as in alkali-graphite intercalation compounds.[32] While K and Rb form a 2×2 structure upon condensation,[31] this order is preceded by an incommensurate 2×2 like structure for Cs.[23,31,33]

The atomic radius of Rb makes this atom fit especially well to the graphene mesh. For Na the structure of an adsorbed monolayer is not known, but the atom is much too small for 2×2 order at full coverage. For adsorbed islands which are 3 ML or thicker the surface layer is a close packed plane of bcc Na but corrugated due to the misfit with the graphene lattice.[34] A possibility is thus that F is characteristic of the 2×2 order. F is then due to a state in graphite, which emits electrons along the surface normal after these have been diffracted by a 2×2 monolayer of alkali metal. A folding of the Brillouin zone shows that the states of interest are found at the six midpoints, M, of the boundaries of the hexagonal graphene zone. One band calculation indicates that the empty σ band along the Γ-M direction has a small negative dispersion such that the energy at M is around 0.4 eV lower than at Γ,[28] another that the energy at M is insignificantly different from that at Γ.[13] An interpretation of the F peaks is then that F_1 and F_2 are due to σ-states near M in the uppermost and next uppermost layers of carbon atoms. Peak F_2 is shifted less than F_1 since the second layer is little affected by the alkali metal. The shift in energy relative to the clean graphite sample for both peaks has two contributions. One is a shift in energy of the entire σ band, say a rigid downshift of the band. The other contribution is given by the difference in band energy between the Γ and M points. We note that our interpretation of the F peaks in terms of diffraction is not possible to verify experimentally by turning the analyzer to probe the final state at the M points. Although the final state is well above the vacuum level the conditions, on energy and parallel wave vector, for escape into vacuum can be fulfilled only if the electrons are diffracted. In an inverse photoemission study the unoccupied σ state was found to have an energy of around 0.8 eV lower at the M point than at Γ.[35] The measured energy at the Γ point is however appreciably higher, 9.5 eV above E_F, than the one obtained in secondary electron emission, 7.6 eV above E_F. Possible reasons for the discrepancy in measured energy with the two different methods are discussed elsewhere.[35,36] Like the absolute energy at the Γ point is different also the measured dispersion between Γ and M would be expected to be different.

Finally we compare the energies of F with the energies of final state peaks observed in photoemission spectra of some alkali metal-graphite intercalation compounds (GICs). In a photoemission experiment on stage 1 potassium GIC (C_8K) Takahasi *et al.*[37] found a prominent peak 6.0 eV above E_F. They interpreted this peak as the final state 7.6 eV above E_F in pristine graphite downshifted by 1.6 eV. In another study by Krieg *et al.*[38] on stage 1 alkali metal GICs a downshift of around 1.5 eV was obtained for C_8M, where M is K, Rb or Cs. Although the shift is in good agreement with the one reported by Takahasi *et al.* the peaks were not as prominent as in Takahasi *et al.*'s measurements.

We note that the energies of the F peaks are nearly the same for K, Rb and Cs. For peak F_1 the energy downshift relative to the final state in pristine graphite is 0.95 eV (Fig. 5). In comparison with the stage 1 alkali metal GIC energy shifts, the smaller shift of the final state reported in this work can be understood from the observed trend of smaller energy shifts for higher stages alkali metal GIC. For example a stage 5 potassium GIC ($C_{60}K$) resulted in a downshift of $\sim$1.2 eV.[38] Our sample, which has just one atomic layer of alkali metal, might be classified as a stage infinity compound.

Peak F_2 in Fig. 3 is ascribed to emission from the final state in the graphene layer next nearest to the alkali metal. This graphene layer is much less affected by the alkali metal, with a peak shift relative to that of clean graphite of only around 0.2 eV. As expected a peak such as F_2 is not observed in the photoemission spectra from stage 1 alkali metal GICs.[37,38]

In measurements on stage 4 potassium intercalated graphite ($C_{48}K$)[38] a shoulder on the high energy side of the final state peak was observed and from the second derivative a split of around 0.7 eV between the two components was obtained. This value is close to the 0.75 eV energy difference between F_1 and F_2 for the K, Rb and Cs/graphite systems (Fig. 5).

V. SUMMARY

In photoemission spectra from graphite recorded along the surface normal there is for photon energies above 12 eV a prominent emission line 7.6 eV above the Fermi level. The line, which is due to a final state in graphite populated by secondary electrons provides via splitting, shift and intensity rather detailed information about the initial stages of growth of alkali metal when evaporated onto a graphite surface.

Upon evaporation of Na, K, Rb or Cs there is an initial rapid decrease of the work function and the peak splits into two components, one of which shifts to lower energy as the deposited amount is increased. The shift is linearly dependent on the work function change, $\Delta E = \alpha \Delta e \Phi$, and the near proportionality between α^{-1} and the radius of the particular alkali metal atom deposited is used for a rough estimate of the DOS near above the Fermi level. In this low coverage range the alkali metal atoms are in a dispersed phase and the alkali metal induced split of the graphite final state is explained in terms of a surface-bulk splitting where the deposition shifts the energy mainly in uppermost carbon layer.

The observed proportionality between ΔE and $\Delta e\Phi$ indicates that a charge transfer and filling of graphite states must be more complicated than what can be handled within a simple rigid band model.

On continued deposition beyond saturation of work function change and shift in energy of the secondary peak there is a marked difference between K, Rb and Cs on one hand and Na on the other. Only for the three heavier alkali metals two new secondary lines appear. The doublet, which is assigned to layer dependent final state energies in graphite, is suggested to be characteristic of the 2×2 order formed by the heavier alkali metals and the new lines would then be due to electrons which have been diffracted by the 2×2 lattice from graphite states at the midpoints of the zone boundary into normal direction.

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