

Condensation of Na metal on graphite studied by photoemission

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Above a submonolayer threshold coverage of around 0.2 monolayer (ML) Na deposited on graphite forms adsorbed islands. Via photoemission from quantum well states (QWS's) the islands are detected down to less than 1% surface coverage and are characterized with respect to thickness via the QWS binding energies. Below 90 K monolayer islands form while at around 110 K the thickness of the initially observed islands is 3 ML. Below 90 K and for coverages slightly above the submonolayer threshold the islands form slowly enough from a dispersed phase that the process can be monitored in real time. Below the threshold coverage the existence of a dispersed Na phase is indicated by the changes of the work function and of the energies for graphite emission lines. One graphite line, which is due to a final state populated by secondary electrons, allows observation of atomic-layer-dependent energy shifts for the substrate. The shifts indicate that Na valence electrons are transferred predominantly to the topmost carbon layer. The work function change and the energy shifts saturate near below the coverage needed for islands to form. The QWS energies for 1 ML Na are well understood in terms of a quasi-two-dimensional free-electron gas having the density expected for a nearly neutral monolayer of Na metal.

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I. INTRODUCTION

As recently demonstrated by photoemission and scanning tunneling microscopy (STM) data, Na metal films on graphite realize simple metal quantum wells in which all filled states are confined and are thus discrete.¹ Although graphite is a semimetal so there is an overlap in valence electron energies, the states in the Na film are decoupled from those in the substrate since the wave vectors are different. The quantum well states (QWS's) in the overlayer form energy bands, which fall well above the highest filled band in graphite throughout the range of wave vectors populated by electrons independent of film thickness. For previously studied metal quantum wells supported by metal or semiconductor substrates, confinement is restricted to a modest fraction of the valence electrons in the overlayer.² The limiting factor is the substrate band gap, which provides the confinement on the back side of the film and typically covers a small fraction of the filled bandwidth of the overlayer metal. Figure 1 shows calculated energy bands of graphite³ with a shaded area representing the range of energies and parallel wave vectors for populated states in Na metal.

Aside from providing prototype examples of simple metal quantum wells Na/graphite is of interest for observing the onset of alkali-metal condensation on graphite and for characterization of the initially formed condensate. This onset has received attention following the observation for K/graphite of a structure change at a low submonolayer coverage from a dispersed phase to a 2×2 ordered K condensate, which above the threshold coverage coexists with the dispersed phase.⁴ A 2×2 structure means that the K atoms are nearly close packed and have the order found also for the K layers in the C_8K intercalation compound.⁵ No similar structure change is observed for alkali metals adsorbed on a metal substrate,⁶ and the difference is ascribed to the semimetal character of graphite.⁷ The experimental data suggested that the condensed 2×2 phase consists of adsorbed K

metal islands.⁸ Electronic structure calculations for the system therefore have been based on the assumption that the condensate is an adsorbed 2×2 K monolayer.⁹⁻¹¹ Recent QWS spectroscopy results indicate that the first formed K condensate instead is a subsurface 2×2 K monolayer.¹² In view of the many previous experimental studies of K/graphite¹³⁻¹⁷ this result is surprising and motivates further investigations of the condensation for other alkali metals.

Na/graphite turns out to be quite different from K/graphite. While Na has a greater tendency for three-dimensional (3D) growth, a low enough substrate temperature (< 90 K) allows a large fraction of the surface to be covered with an adsorbed Na metal monolayer. The appear-

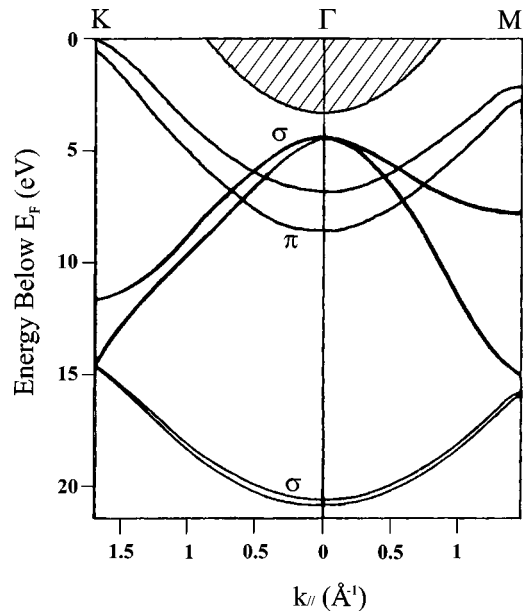


FIG. 1. A calculated band structure of graphite (Ref. 3) with a shaded area enclosed by the dispersion of Na valence electrons in the free-electron approximation.

ance of Na islands can be monitored via the photoemission of electrons that occupy QWS's. These have thickness-dependent binding energies, which means that the island thickness can be determined unless many different thickness values are represented. We observe QWS characteristics of Na adlayers above a submonolayer threshold coverage. This result suggests that Na/graphite can provide an example of the transition from a dispersed to a condensed alkali-metal adsorbate on a semimetal.

Regarding the low-coverage dispersed phase our data give only indirect information about the Na adsorbate. We observe no emission lines that can be ascribed to the Na valence electrons, and the $2p$ line is not well resolved within our photon energy range since the line is superposed on a large background of secondary electrons. The indirect information comes from the change of the work function and the shift in binding energy of graphite emission lines as Na is deposited. Initially these quantities change gradually with increasing Na deposition time but then saturate at a slightly lower coverage than required to observe QWS emission out of Na metal islands. As discussed below the results obtained at low coverage are well understood in terms of a dispersed Na adsorbate.

II. EXPERIMENT

The measurements were made using as substrate samples of highly oriented pyrolytic graphite (HOPG). This consists of microcrystals which have a nearly common c axis but which are azimuthally disordered. The disorder means that in low-energy electron diffraction (LEED) the pattern consists of rings rather than spots. In one experiment an epitaxial graphite layer formed *in situ* by heating SiC (Refs. 18 and 19) was used as substrate. The photoemission spectra are recorded in the MAX synchrotron radiation laboratory, Lund University, at BL52 where a normal incidence monochromator provides photons in the energy range from 3.5 to 40 eV. The alkali metal is evaporated from a heated breakseal ampoule, which is kept at constant temperature typically set to give a monolayer within 3–10 min. With HOPG as substrate a temperature of around 40 K is reached with LHe and around 90 K with LN₂. During an experimental run the temperature is checked with a thermocouple clamped to one end of the sample. The temperatures given above were obtained from a calibrated diode, which was attached to the sample after one of the experiments. The holder used for the SiC sample gave a lower-temperature limit of around 100 K.

III. RESULTS

A. Low Na coverage

At low Na coverages, less than 0.2 monolayer (ML), the work function decreases rapidly with increasing deposition time and emission lines due to the substrate shift to gradually lower energies. Both changes saturate at approximately the same coverage, which marks the limit of a low-coverage range (1 ML is the coverage of a full Na monolayer, and if, as discussed below, this is a close-packed bcc plane, the number of C atoms per Na atom is ~ 5). The work function

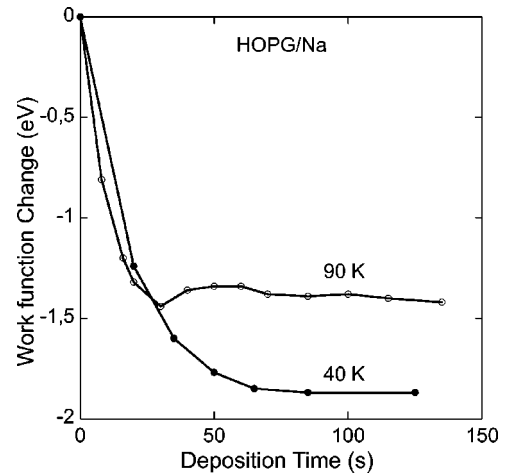


FIG. 2. Work function change vs Na deposition time for two different sample temperatures. The minimum for 90 K at ~ 30 s is due to a temporary oversaturation of the dispersed phase. At 40 K, island formation proceeds more slowly, allowing a larger reduction of work function.

change, which is obtained from the low-energy cutoff of photoemission spectra, depends on temperature (Fig. 2). At 90 K the change also depends on how rapidly the coverage dependence is measured. As discussed in Sec. IV C a rapid measurement gives a lower work function due to a temporary oversaturation of the dispersed Na phase characteristic of the low-coverage range. The weak minimum in Fig. 2 for 90 K is thus only observed if the coverage dependence is measured in a few minutes time or less.

The spectra recorded along the surface normal show graphite emission lines which all shift to lower energy upon Na deposition; i.e., filled states shift towards higher binding energies and states above the Fermi level shift towards this. Most detail is given by an emission peak, which is due to a state 7.6 eV above the Fermi level populated by secondary electrons. This emission peak has been observed previously^{20,21} and was ascribed to a σ state.²⁰ Particular with this peak is that it splits into components upon Na deposition with one component remaining at constant energy. The splitting suggests that the escape depth of the electrons is sufficient to allow observation of atomic-layer-resolved energies for the substrate. In Fig. 3 two components are seen clearly and for the highest Na coverage a shoulder on the low-energy side of the stationary component indicates a third component. The splitting ΔE of the two main components is linear with the change in work function, $\Delta E = 0.44\Delta e\Phi$.

Another final state is observed only after deposition of a small amount of Na. For clean graphite this state lies near the vacuum level and is therefore revealed only after a reduction of the work function. In previous work the state has been observed by inverse photoemission²² and with near-edge x-ray-absorption fine structure²³ (NEXAFS). Although the state can be monitored in a restricted Na coverage range, also this state shifts and at saturation the energy is around 4.3 eV above the Fermi level. As discussed below this state is of interest for the interpretation of spectra recorded at 1 ML thickness. The upper filled σ state in graphite (Fig. 1) gives

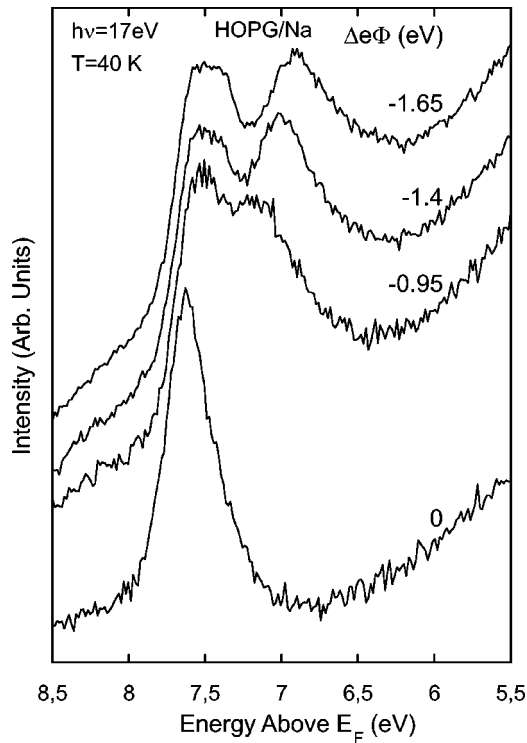


FIG. 3. Na adsorption induced splitting of a secondary emission peak due to a state in graphite 7.6 eV above E_F . The splitting ΔE is proportional to the work function change $\Delta e\Phi$, which is given for each spectrum.

an emission line which shifts in energy but also broadens. Although the broadening makes the shift less well defined, it is not significantly different from the shift observed for the state 7.6 eV above E_F .

B. High Na coverage

If the deposition is continued beyond the saturation of the work function, emission peaks characteristic of QWS's in Na films and islands are observed. Spectra for 1 ML Na show two populated states at the center of the Brillouin zone, at 0.17 eV and 1.65 eV binding energy, respectively (Fig. 4). As explained in Sec. IV A the peaks are labeled with the number of nodes, m , the states have in the overlayer.¹ Low photon energies are used since the cross section is strong only at photon energies in the vicinity of the plasmon energy, (5.7 eV for Na) or lower than that.^{24,25} As the photon energy is increased and the QWS intensity becomes weaker emission from the substrate is observed. An example of this is the peak labeled *S* in Fig. 4. This peak is due to the final state 4.3 eV above the Fermi level mentioned in Sec. III A. The intensities in Fig. 4 are compared with reference to the current in the storage ring. This is an acceptable reference since the light from the monochromator has a flat intensity in this spectral range compared to the strong variations of the QWS intensity.

The QWS emission appears at a coverage slightly higher than required for saturation of the work function. The high intensity of the peak at 0.17 eV binding energy is useful for

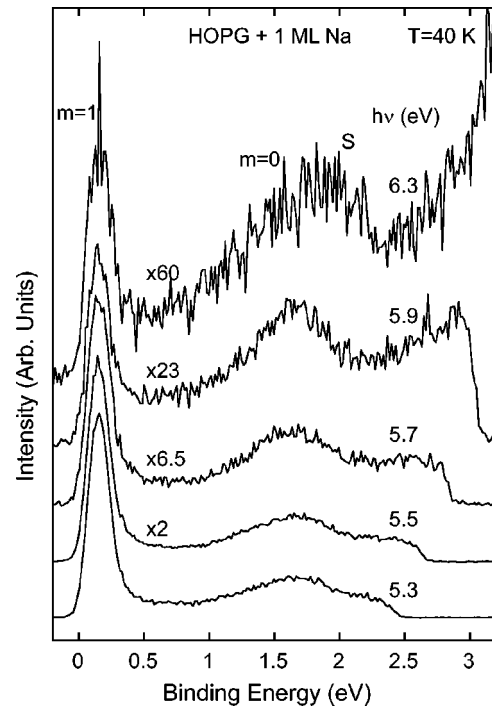


FIG. 4. Photoelectron energy spectra recorded along the surface normal for 1 ML Na on HOPG show emission peaks due to states 0.17 eV ($m=1$) and 1.65 eV ($m=0$) below E_F . The peak, at 2.0 eV, labeled *S* in the spectrum obtained at $h\nu=6.3$ eV is due to a final state 4.3 eV above E_F . Note the decrease in intensity as the photon energy is increased.

observing the onset of island formation. At the lowest coverages for which the state is observed the emission peak appears with some delay after the deposit. Figure 5 shows the development with time after a deposit made with the sample held at 90 K. The intensity saturates after around 10 min. In the case shown the intensity is around 0.5% of the maximum intensity for the 1 ML state. The increase of the QWS intensity is accompanied by an increase of the work function observed in Fig. 5 as a shift of the low-energy cutoff of the spectrum. The difference between the work function curves in Fig. 2 is thus explained by the time it takes for the Na atoms to reach an equilibrium arrangement. For larger deposits the QWS emission is present immediately after the deposition and the delay is less apparent.

Assuming a constant Na sticking probability the deposition time required to saturate the work function divided by the time it takes to obtain maximum intensity for the QWS characteristic of a monolayer gives a saturation coverage of 0.2 ML. Another uncertainty in this value is that the surface may not be fully covered with a monolayer before there are patches with thicker Na metal. Judged by the QWS emission intensity the largest surface coverage is obtained with the sample temperature in the range between 40 and 90 K. At 40 K the film is disordered while at 90 K there are 2-ML-thick areas before the monolayer is complete. The thickness of the initially formed islands is well defined but depends on the temperature. At 90 K monolayer thickness is preferred whereas at somewhat higher temperature (110 K), the first

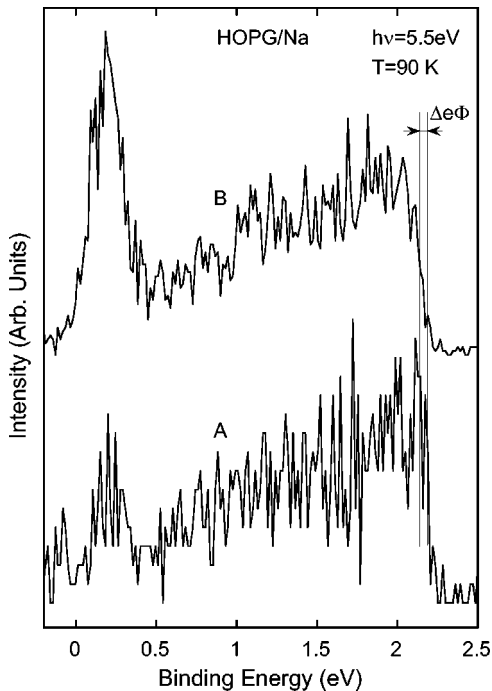


FIG. 5. Photoelectron energy spectra recorded along the surface normal for Na/HOPG at a coverage slightly higher than the threshold coverage for Na metal condensation. Spectrum A is recorded immediately after deposition and B 10 min later. The peak at 0.17 eV binding energy is characteristic of 1 ML islands. The island formation is accompanied by a small increase of the work function, $\Delta e\Phi$.

formed islands are 3 ML thick. The thickness is determined via the QWS binding energies.¹

The temperature dependence of the thickness is exemplified in Fig. 6, which gives characteristic emission lines at 0.7 eV and 0.9 eV characteristic of 3 and 4 ML thickness respectively¹ (bottom spectrum). When the cooling is interrupted and the temperature increases, the emission characteristic of the 4 ML thickness increases while the emission characteristic of 3 ML Na decreases. The change is not accompanied by any emission characteristic of 1 or 2 ML thickness, which means that there must be areas with clean graphite or more likely areas covered with dispersed Na atoms. As the temperature is increased further lines characteristic of 5 and 6 ML thicknesses are observed. In a previous study of morphological changes via QWS spectroscopy, Luh *et al.*²⁶ observed that N -atomic-layer-thick Ag overlayers on Fe(100) can bifurcate upon a temperature increase into $N \pm 1$ monolayer thickness. For the present system we observe only a change to larger thickness as the temperature is increased.

IV. DISCUSSION

A. QWS's for Na/graphite

Ideal as samples for a study of QWS's would be thin unbacked films. In such films all electrons are confined and have discrete energies determined by the potential in only one substance. For photoemission experiments, when a con-

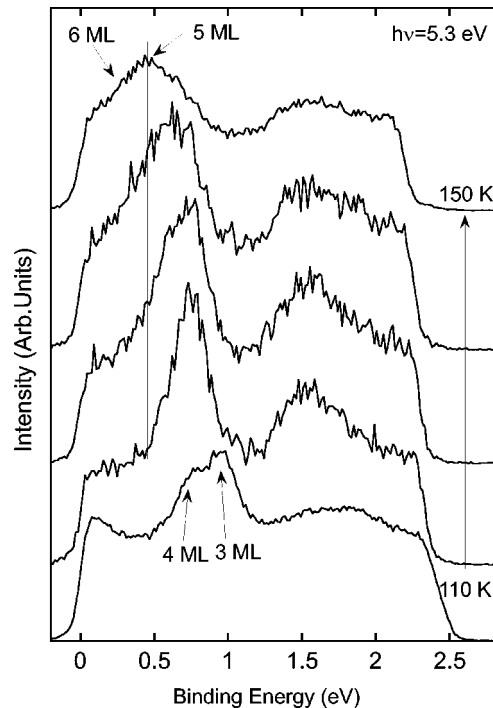


FIG. 6. Morphological change with gradually increasing temperature for a Na film with 3-ML- and 4-ML-thick areas (bottom spectrum). With increasing temperature, islands with 5 ML and 6 ML thickness form.

ducting sample is needed, the next best choice may be a film backed by graphite since this provides confinement over a wide range of energies and parallel wave vectors. A simplified picture of the situation for Na/graphite is given in Fig. 1 which shows the energy bands of graphite and the free-electron dispersion for a metal with the density of Na. All occupied valence states in a film of this metal are expected to fall within the area (shaded in Fig. 1) enclosed by the free-electron parabola. Within this area the substrate lacks states and a state in the film can extend on the substrate side of the interface only with a tail. Every state in the film is therefore expected to be discrete and characterized by a perpendicular wave vector component k_{\perp} , given by the quantization rule $2k_{\perp}t + \Phi = 2\pi m$, where $t = Nd$ is the thickness of a film consisting of N atomic layers each with thickness d , Φ the sum of the phase shifts at the vacuum barrier and the interface, and m a quantum number, which is here chosen to be the number of nodes in the film.²⁷

A simplification made in Fig. 1 is that the graphite bands are unperturbed by the contact between the two solids though the Fermi level is common. In reality this level becomes common via a transfer of electrons to the substrate, the energy levels of which are downshifted in the uppermost graphene layers. The shifts are not large enough to be of consequence for the discussion above regarding the confinement. Another simplification is neglect of the fact that the states in the film have tails in the substrate and therefore sense the lateral variation of the substrate potential. This may be expected to affect the band mass for the lateral dispersion of the QWS and introduce band gaps at the lateral boundaries of the graphite Brillouin zone. As shown in Fig. 1 these

boundaries are, however, remote from the range of k_{\parallel} values populated by the QWS's. Likewise neglected is the influence of the periodic potential in the overlayer on the propagation of the electrons in the substrate. In principle the folding of the graphite zone caused by the spatial period in the film could be important for the present experiment since it means that substrate electrons may be emitted in new directions. The reason for neglecting this diffraction effect is that we have found no evidence of it in the measured spectra.

B. Low Na coverages

The breakpoint in the coverage dependence of the work function from an initially rapid to a much slower change as the deposition is continued serves as a demarcation between two different coverage regimes. For coverages below the breakpoint the photoemission is dominated by the substrate states at all photon energies employed. The emission lines are downshifted gradually as the deposition time is increased. Our observations are restricted, however, to σ states, the upper filled one and one 7.6 eV above the Fermi level. The shift of the filled σ state is somewhat smaller than for the empty one, but since the emission line broadens upon adsorption, it is unclear whether the difference is significant. The secondary peak due to the state 7.6 eV above E_F in graphite is particularly interesting since it is only for this a splitting is observed upon Na deposition. We associate the splitting with bulk-surface split energies. Support for this is given by the fact that one of the components remains at nearly constant energy. At the highest coverage shown in Fig. 3 the stationary component has a shoulder on the low-energy side which suggests that a shift, by 0.2 eV, is resolved for the second graphene layer. For σ states, layer-defined and depth-dependent binding energies may be expected due to a small overlap between σ states in adjacent atomic layers. Typically depth-dependent binding energies can be observed for core levels, but in the case of K/graphite the C 1s line did not reveal this as clearly as the secondary peak 7.6 eV above the Fermi level.¹⁷

The work function change can be regarded as the sum of two contributions. One is the decrease due to the downshift, E_s , of the energy bands in the top graphite layer and the other the drop due to the potential difference, U , between this layer and the layer of adsorbed Na atoms. If the charge transferred to the two topmost carbon layers is q_1 and q_2 , respectively, and the transfer to deeper layers is neglected one obtains, using the parallel plate capacitor expression for U , that $\Delta e\Phi = E_s + d(q_1 + q_2)/A\epsilon_0$, where d is the distance between the Na and the top carbon layer. If a value of q_1 is obtained from a rigid shift by E_s of the calculated density of electron states near the Fermi level,^{17,28} the measured shift $E_s = 0.8$ eV gives a charge transfer to the uppermost graphite layer of 0.008 electrons per carbon atom, which at 0.2 ML coverage means that each Na atom has lost $0.2e$. When this procedure was used to obtain the charge transferred from K atoms on HOPG (Ref. 17) at the saturation coverage for the dispersed phase a similar value was determined ($0.18e$ per K atom). We believe, however, that a correct evaluation gives

$0.36e$, taking into account the spin degeneracy of the calculated density of states used for obtaining the charge transfer.

A reason for caution regarding the charge transfer values obtained from a rigid density of states is that the observed linear relationship between the binding energy shift and the work function change, $E_s = 0.44\Delta e\Phi$, is not explained. The density of states is approximately linear near its deep minimum at the Fermi level.^{17,28} A shift in energy by E_s therefore corresponds to accommodation of a charge proportional to $n(E_F)E_s + \alpha E_s^2$. This charge enters the second term of the expression for the work function change, and a linear dependence on E_s is obviously not expected.

A possible reason for the discrepancy is that the density of states function in the uppermost graphene layers is significantly altered due to the adsorbate such that the deep minimum near the Fermi level is no longer present. Although the observed downshift of σ states upon adsorption signals a rigid band shift, this may not apply to the π states near the Fermi level, which are of main interest for the charge transfer. These are found near the vortices of the Brillouin zone. So far it is only for clean graphite that some of the details of the intricate band structure near the zone corners have been resolved by photoemission.¹⁸ While graphene is a zero-gap semiconductor the 3D structure introduces a splitting of the π states and this makes graphite a semimetal. The bulk character of the states near E_F , or some of them, suggests that they could respond to adsorption in the manner of bulk states in metals: no shift in energy but an altered amplitude near the surface due to the changed surface boundary condition. This is in contrast to surface states which can shift in energy and occupancy upon adsorption and thereby participate in establishing the new charge balance at the surface.^{29,30} Although the σ states in graphite do shift in energy, the occupancy is not changed since no σ band crosses the Fermi level.

Another reference of interest is a semiconductor with surface band bending. In that case bulk states have different energies at the surface and in the bulk. The band structure concept remains valid since the bending region typically extends deep into the solid and the shift in energy within a unit cell is insignificant. Photoemission spectra, which probe a shallow surface layer, then merely shift in energy, by E_s , when the band bending is quenched by lowering the temperature and/or increasing the light intensity enough to saturate the surface photovoltage.^{31,32}

In the present case the observed energy shifts show that only the two uppermost carbon layers are appreciably affected by the adsorbate. The unit cell of graphite contains atoms in two carbon layers, so the perturbation is not uniform within the cell. Furthermore, the shift in energy between the layers is on par with the band splitting, which means that the adsorbate-induced change cannot be regarded as a weak perturbation. Also in the lateral direction the adsorbate will introduce a nonuniform perturbation that may make more diffuse such distinct details as the deep density of states minimum in graphite near the Fermi level. The suggestion is thus that the band picture is irrelevant to describe the electronic structure near the Fermi level in the two uppermost layers of an alkali-metal-covered graphite substrate.

C. Na metal condensate

The spectra recorded for 1 ML at 90 K is as expected for a near neutral monolayer of free-electron metal with the density of Na. Since no solid is thinner than a monolayer, this overlayer might be expected to provide the best example in nature of a 2D free-electron-like gas with metal density. For such a gas the filled bandwidth W is given by $W = nh^2/4\pi m$ where n is the surface density of electrons and the density of states, $n(E)$, is constant and equal to $4\pi m/h^2$. For a monolayer of close-packed Na atoms with the interatomic distance equal to that in bcc Na one obtains $W = 2.06$ eV. This is close to the bandwidth 2.12 eV, obtained in a band calculation for a monolayer of close-packed Na atoms in vacuum.³³

Atom-resolved STM images for 3 ML and thicker Na islands show a buckled bcc (110) surface.¹ If this is the order also for 1 ML, the free-electron approximation gives $W = 1.89$ eV. In a photoemission spectrum recorded along the surface normal one would expect to observe one emission peak at a binding energy equal to W . Instead the monolayer gives two peaks (Fig. 4), which means that not only the bottom $m=0$ level, but also the next higher one $m=1$ is occupied near the center of the Brillouin zone. Even this film is thus too thick to be representative of a true 2D electron gas where the electrons are confined to a plane and only one band exists. The zone center states mark the low-energy edge of subbands, which each gives the same contribution to the density of states. The density of states at the Fermi level is thus twice that of the ideal 2D gas. The sum of the observed QWS binding energies is 1.82 eV, which is close to the bandwidth for the 2D gas. While the difference may be ascribed to a band mass larger than 1 the smaller value for the combined width also leaves room for a small charge transfer, (around $0.04e$ per Na atom), from the adsorbed layer to the substrate. For the states on the receiving end of the transfer this means 0.008 electrons per C atom if all electrons are accommodated by the uppermost atomic layer in graphite. This amount of charge is the same as that at saturation of the work function and consistent with the observation that the shifts of graphite levels saturate at this coverage.

At 90 K the condensation of the Na atoms into metal monolayer islands proceeds slowly enough that it can be monitored in real time as shown in Fig. 5. The lack of any shift in binding energy suggests that, when detected, the islands have areas large enough that lateral quantization is of little importance for the QWS energy. Since the experimental resolution would allow us to observe a shift of 50 meV, an estimate of the area suggests that these have lateral dimensions of around 100 Å. If the islands form from an oversaturated phase of dispersed Na atoms, the early stage of agglomeration into small islands is thus not detected. The reason for this is not clear but it could be associated with the excitation mechanism. The emission intensity from ultrathin or thick samples of free-electron-like metals is strong below the plasma frequency due to the excitation of collective modes.^{24,25} How the modes are damped, and the characteristic frequencies changed as the lateral dimensions are reduced for an ultrathin island is not known.

As implied by the phase condition satisfied by QWS's the level structure is expected to be similar for different alkali metals on a given substrate if the number of adsorbed atomic layers is the same. Adsorbed on Cu(111) 1 ML of Li, Na, and Cs in all cases gives a filled $m=1$ state at Γ within 0.14 eV of E_F .³⁴⁻³⁶ According to our interpretation of the present results this state has a binding energy of 0.17 eV for Na on graphite. An energy near this value is then expected also for K-covered graphite, but the first K-deposition-induced Γ level has a binding energy of 0.57 eV.¹² It is only after deposition of a second K atomic layer that the level spectrum is similar to that obtained for 1 ML of Na. The thermal stability of the first formed condensate is also quite different for K and Na. While the Na monolayer can be prepared only below around 90 K the temperature can be raised to around 200 K for K before the Γ level with 0.57 eV binding energy disappears. It is then not replaced by QWS's characteristic of thicker islands which is typical of Na films. Aside from the energy another important signature of QWS's is the cross section. For 1 ML of Na this is enhanced at low photon energies as previously observed for Na both on graphite or on a metal substrate.^{1,2} In the case of K the characteristic photon energy dependence of the cross section is observed only after deposition of the second atomic layer. In addition the splitting of the 7.6 eV state upon deposition (Fig. 3) is followed for K by a stepwise shift upon continued deposition.¹² There are thus a number of differences between the two surface systems. For K the suggested interpretation is that the initially formed condensate is a subsurface monolayer.¹² For Na the results are consistent with a change from a dispersed low-coverage phase to a condensed phase of adsorbed islands which have monolayer thickness if the temperature is below around 90 K but thicker at higher temperature.

V. CONCLUDING REMARKS

The results show that QWS spectroscopy provides a sensitive means of observing the formation of a condensate by adsorbed metal atoms. In the Na/graphite case QWS characteristics of adsorbed alkali-metal islands are observed only when a submonolayer threshold coverage is exceeded. Below threshold a dispersed phase is indicated by the work function change and shifts of substrate energy levels. The behavior gives support to a theoretical model which ascribes the existence of a threshold coverage for condensation to the semimetal character of the graphite substrate.⁷ Although the islands formed at low enough temperatures have the ultimate monolayer thickness, the electronic structure deviates markedly from that of a true 2D electron gas since two subbands are occupied rather than one. For a freestanding monolayer, by contrast, calculations predict that only one subband extends below the Fermi level.³³

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