Phase Transitions and Excitation Spectrum of Submonolayer Potassium on Graphite

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(Received 7 March 1991)

We have investigated both the structures and the excitation spectra produced by submonolayer adsorption of potassium on the surface of graphite at 90 K, using high-resolution LEED and electron-energy-loss spectroscopy. We show that at very low coverages a dispersed potassium phase is formed with a giant K-K spacing (around 60 Å); this phase continuously compresses with increasing adatom density until a critical coverage where a close-packed structure nucleates. Below the critical coverage, charge is redistributed between the alkali and the substrate to increase the frequency of the substrate plasmon mode; above the critical coverage, excitations attributed to metallic potassium are observed.

PACS numbers: 68.55.Nq, 61.14.Hg, 73.20.Dx, 79.20.Kz

The adsorption of alkali metals on solid surfaces is a classic problem in surface physics. The relative simplicity of the electronic structure of the alkalis makes the adsorption of these elements a touchstone for our understanding of bonding and structure of atoms at surfaces [1,2]. Two questions are currently the topic of lively debate [3]: (i) What is the nature of the alkali-surface bond at the lowest coverages? (Is there charge transfer to the substrate?) (ii) What is the density at which the alkali layer becomes metallic? An appealing route towards further experimental progress in addressing these questions is the application of a combination of structural and spectroscopic probes to a given system, so that a solid correlation can be established between particular structures and their characteristic excitation spectra, the latter being sensitive to the distribution of electronic charge in the system. In this Letter we report a study of submonolayer potassium adsorption on the surface of graphite with high-resolution low-energy electron diffraction (LEED), for structural characterization, and high-resolution electron-energy-loss spectroscopy (EELS), to determine the excitation spectra. We choose graphite as the substrate because the low density of states at the Fermi level of this semimetallic material suggests that the excitation spectrum of the substrate will be especially sensitive to charge transfer from the alkali. Recently, both distinctive electron-hole-pair [4] and plasmon [5] excitations of graphite have been isolated, which manifest the semimetallic nature of the material. The potassium/graphite system is also of interest as a prototypical intercalation compound [6]. In addition, an understanding of the physics of the alkali-graphite interaction may also be a vital resource in developing an understanding of the newly discovered alkali-doped C_{60} fullerene superconductors [7].

We find that at the lowest alkali densities on the surface of graphite a dispersed potassium phase is formed with a giant K-K spacing, clearly manifesting a repulsive K-K interaction. The low-frequency graphite plasmon mode is substantially shifted up in energy, which is a hallmark of charge redistribution involving the band structure of the substrate. As the adatom density increases, the K-K spacing in the dispersed phase is compressed continually and the plasma frequency rises monotonically until a critical coverage is reached, whereupon a coexisting close-packed 2×2 K phase begins to grow until it covers the whole surface. The close-packed phase is marked by no increase in the graphite plasma frequency, implying that charge redistribution is confined to the two-dimensional K layer, and hallmarked by a set of excitations which can be qualitatively assigned to transitions within the band structure of two-dimensional metallic K islands.

The experiments were performed in an ultrahigh-vacuum chamber with a base pressure of 3×10^{-10} mbar. K was evaporated using a thermal getter source onto the surface of a piece of highly oriented pyrolitic graphite (HOPG) (Ref. [6]), prepared in the manner previously described [4,5]. The azimuthal randomness of the grains in the surface of HOPG means that rings, not spots, are observed in LEED. The sample was mounted on a cryogenic cold finger [8] and cooled to a temperature of about 90 K. Low temperatures are necessary because at room temperature we find that K intercalates into the graphite bulk [9]. Measurements were made with an EELS spectrometer which can also be used to obtain high-resolution one-dimensional LEED profiles [10].

Figure 1(a) presents a sequence of LEED profiles obtained with an electron-beam energy of 9 eV as a function of increasing (but low) coverage of K on the surface, labeled in terms of the corresponding evaporation time. One particular feature is clearly seen in the scans in addition to the (0,0) diffraction beam: a discrete diffraction peak which moves out to higher wave vector (q) as the coverage increases. No other substantial adsorbate-derived features are seen in the LEED scans in this coverage regime. A number of previous LEED studies [2] of alkali adsorption on various surfaces, using conventional apparatus, have identified a diffuse ring in the LEED patterns which shifts to higher wave vector with increasing coverage. Conventionally, such a feature is taken as evidence for a repulsive alkali-alkali interaction at low coverage, leading to large spacings between the adatoms [1,2]. At still lower coverages we have been able to clearly resolve a diffraction peak at a wave vector as small as 0.1 Å^{-1} (much smaller than seen in previous studies of

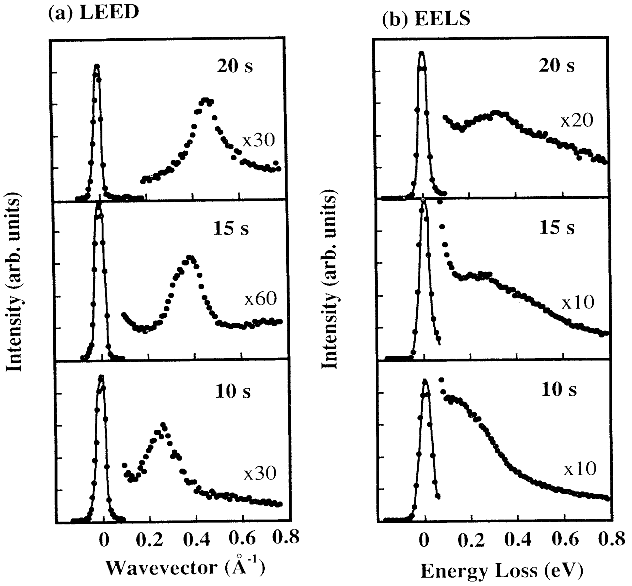

FIG. 1. (a) LEED profiles and (b) HREELS spectra (specular geometry) for low coverages of potassium on graphite. Evaporation times are labelled. Electron-beam energy, 9 eV; angle of incidence, 60° from the normal in each case.

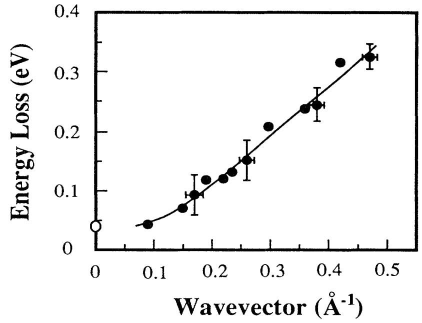

FIG. 2. Experimental plasmon frequency as a function of the position of the low-q diffraction peak in the low-coverage regime. The solid line is a guide to the eye. The theoretical plasmon frequency of clean graphite (Ref. [5]) is also plotted.

alkali adsorption), corresponding to an extremely large K-K spacing of around 60 Å. The repulsive interaction between adatoms is generally thought to arise from dipole-dipole repulsion [1,2] (dipole formation accounts for the large decreases in the substrate work function which are observed upon alkali adsorption). As the density of adatoms is increased, the distance between adatoms is forced to contract. The continuous shift to higher wave vector of the diffraction feature we observe is direct evidence of a continuously compressing dispersed potassium phase. Whether this structure is a solid or strongly correlated liquid [2] we cannot say.

Of special interest is the relationship between the observed structure and the electronic excitation spectrum of the system, since the latter will be sensitive to the redistribution of alkali charge upon adsorption. Figure 1(b) shows a sequence of EELS spectra corresponding to the LEED scans of Fig. 1(a). Each EELS spectrum was acquired immediately before the relevant LEED data set. As in the LEED data, a single feature is clearly evident in the EELS spectra [Fig. 1(b)]: A loss peak which moves out to higher energy as the coverage is increased, ultimately reaching an energy of around 320 meV. Recently, Jensen *et al.* [5] reported the observation of a low-frequency plasmon in the EELS spectrum of clean graphite, whose frequency was found to be a function of temperature. The clean-graphite plasmon was not observable at 90 K, but calculation [5] indicates that its frequency at that temperature is about 40 meV. The temperature dependence arose because of thermal population of the conduction band with carriers in the semimetallic band structure. It was conjectured that similar shifts in the plasma frequency might be induced by the adsorption of dopants on the surface of graphite. The data presented in Fig. 1(b) certainly accord with this idea. As the density of alkali on the surface increases, and the adatom-adatom distance contracts, the mode observed in Fig. 1(b) shifts up in frequency, as would be expected of the surface-plasmon mode if charge is being redistributed from the adsorbate towards the substrate. Thus we assign the loss feature of Fig. 1(b) to a frequency-shifted (perturbed) graphite plasmon.

In Fig. 2 we plot the frequency of the observed low-energy loss peak as a function of the wave vector of the low-q peak in the LEED scans. The data for Fig. 2 are assembled from a large number of spectra of which those shown in Fig. 1 are examples. On the assumption that the symmetry of the adsorbate structure remains constant while it is being compressed, we can interpret q as being proportional to the square of the alkali coverage (direct determination of the coverage from the evaporation time is difficult because of drifts in the evaporator parameters). The data presented in Fig. 2 confirm a clear correlation between the frequency of the loss peak, assigned to the plasmon mode, and the coverage of K on the surface. This leads us to believe that at low coverage there is a distortion of the electronic charge density of the alkali atom such that it overlaps with that of the substrate. If one is willing to assume that the band structure of the graphite substrate is unperturbed by the adsorption of alkali (a presumption which appears to work quite well in the case of graphite intercalates, Ref. [6]), it is possible to work out the amount of charge transferred per K atom, given that the calculated density-of-states function of graphite is available in the literature [11]. On the other hand, it is possible that the band structure of the substrate could be perturbed by adsorption, at least locally. In our view one ought to be cautious about interpreting the data presented as being in support of the notion of charge *transfer,* but one can certainly conclude that there is a *redistribution* of alkali charge which involves the graphite substrate, and which increases (from the alkali layer as a whole) with increasing alkali coverage in the low-density regime.

As the coverage of K on the surface is increased beyond the regime represented by Figs. 1 and 2, marked qualitative changes occur in both the LEED and EELS data. In particular, there is a critical coverage θ_c at which the wave vector of the diffraction feature of Fig. 1(a) ceases to increase further (maximum value around 0.45 $Å^{-1}$, corresponding to a K-K separation of about 14 Å), and, simultaneously, the plasma mode of Fig. 1(b) ceases to increase further in energy (maximum value about 320 meV). From this point new features manifest themselves in both the LEED and EELS data. In the LEED profiles [Fig. 3(a)], the low-q peak is first joined by a second peak at $q = 1.7$ $Å^{-1}$, which quickly gives way [12] to a peak at 1.5 $Å^{-1}$, the latter growing steadily in intensity as the 0.45-$Å^{-1}$ peak decays away. The wave vector of the 1.5-$Å^{-1}$ peak corresponds to the close-packed 2×2 structure previously observed in alkali-metal adsorption on graphite [13], and also to the in-plane structure of various graphite intercalation compounds, including the K/graphite system [6]. The growth of the 1.5-$Å^{-1}$ peak at the expense of the 0.45-$Å^{-1}$ peak is interpretable in terms of the nucleation and growth of close-packed 2×2 islands which spread over the surface as the coverage increases.

At the same time that the close-packed islands grow over the surface of the substrate, new excitations clearly characteristic of this phase manifest themselves in the EELS spectra [Fig. 3(b)]. Three loss peaks increase in intensity as the intensity of the plasma mode dies away, at 1.2, 1.5, and 2.2 eV. A detailed assignment of these peaks would require a calculation of the electronic band structure of two-dimensional K, but enough can be said to justify the qualitative conclusion that these excitations are indeed indicative of a metallic state. Consider first the potassium atom, which has a sequence of familiar dipole transitions involving the outermost valence electron in the 4s level. The lowest-energy transition [14] is at 1.6 eV (4s-4p), quite close to the 1.2- and 1.5-eV peaks observed in Fig. 3(b). In a two-dimensional metallic band structure derived from the atomic K levels one might expect the degeneracy of the 4p level to be split such that the (in-plane) $4p_x$- and $4p_y$-derived bands are split from the (out-of-plane) $4p_z$-derived band [15]. We conjecture that the two transitions at 1.2 and 1.5 eV in Fig. 3(b) might represent transitions between the 4s-derived band and this pair of split bands. We speculate that the 2.2-eV feature arises from another single-particle interband transition or the "work-function" threshold excitation recently predicted by Ishida and Liebsch [16]. Most significantly, the absence of a further shift in the frequency of the plasmon mode and its decay in intensity as the 2×2 phase grows indicates that the frequency-shifted graphite plasmon excitation is a characteristic of the dispersed phase, and not the close-packed phase. Thus the charge redistribution involving alkali and substrate which leads to the frequency shift of the graphite plasmon at low coverage does not occur in the close-packed phase. This is consistent with a redistribution of charge (i.e., metallic bonding) within the close-packed layer, rather than to the substrate, in the 2×2 structure.

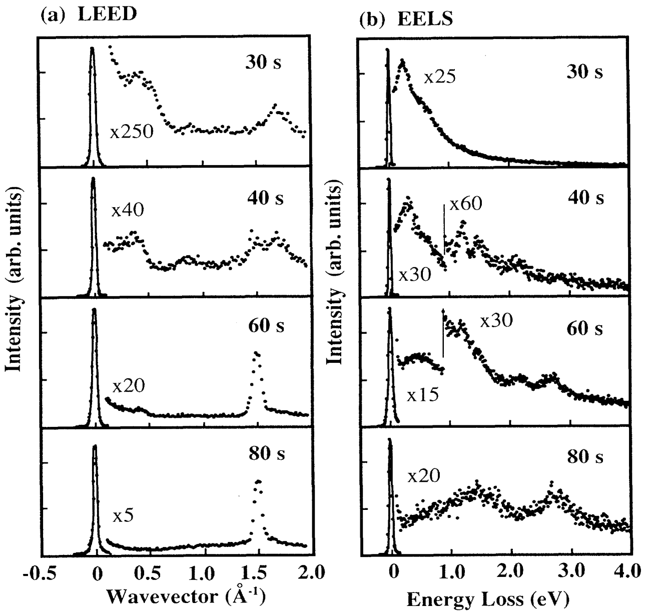

FIG. 3. (a) LEED profiles and (b) HREELS spectra (specular geometry) for higher coverages of potassium on graphite. Evaporation times are labelled. Evaporation source conditions are different from Fig. 1. Electron-beam energy, 19 eV; angle of incidence, 60° from the normal in each case.

One further aspect of the transition between the dispersed phase and the close-packed phase in the system which is worthy of emphasis is the fact that the compressing phase does not match smoothly onto the close-packed structure. One can understand this on a basis where the repulsive energy between polarized adatoms is rising as they are pushed closer together while the density is increasing. Once they reach a certain distance apart the repulsive energy cost becomes exorbitant and it is energetically more favorable for close-packed islands to grow and displace the dispersed phase than for the dispersed phase to compress further. This is one of several aspects of the present results which might repay a detailed theoretical treatment in the future.

Finally, we note that as the coverage continues to increase the sharp 2×2 diffraction peak weakens and broadens, indicating the growth of a disordered film at higher coverages (almost certainly in the multilayer regime). At the same time the loss features characteristic of the close-packed structure dwindle in intensity and are replaced by a single broad loss [already evident in Fig. 3(b)] at a frequency, 2.7 eV, close to the surface-plasmon frequency of bulk K, as previously observed in thick, polycrystalline alkali films [17].

In summary, we have shown that, as a function of coverage, submonolayer K on graphite undergoes a structural phase transition from a dispersed, low-density phase, characterized by alkali charge redistribution involving the substrate and repulsive adatom-adatom interactions, to a close-packed, high-density metallic phase which appears to leave the graphite band structure at least largely unperturbed. Finally, it is interesting to speculate whether phenomena similar to those reported here in the very-low-coverage regime may also be observable in the very early stages of intercalation in graphite [6], as well as in alkali adsorption on other semimetallic or narrow-band-gap systems, where strong perturbations of the substrate excitation spectrum arising from charge redistribution might again be expected.

We are thankful to Professor J. F. Annet, Professor B.Y. Gyorffy, and Dr. M. C. Payne for helpful discussions. Financial support by the Royal Society is gratefully acknowledged. K.M.H. thanks Caius College, Cambridge, for financial assistance.

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