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Abstract. A discrete energy loss feature has been observed after adsorption of small amounts of potassium on graphite at 90 K, the frequency of which increases markedly from about 50 meV at the lowest potassium coverage to 320 meV at a coverage of 0.1 ML. This feature is attributed to a surface plasmon mode. The shift in plasmon frequency allows an estimate, within the framework of a rigid band model for the graphite substrate, of the amount of charge transfer from the potassium layer as a function of coverage.

1. Introduction

Recently Jensen *et al* reported the observation of a low frequency plasmon in the high-resolution electron energy loss spectrum (EELS) of clean graphite, whose frequency was found to be strongly temperature dependent [1]. The authors attributed the effect to the thermal population of the conduction band with carriers, in the semimetallic band structure. They also presented a theoretical band structure calculation which proved to be very successful in describing the temperature dependence of the plasmon frequency. The same calculation also predicted that similar shifts in the plasmon frequency would arise from a shift of the Fermi level, which the authors speculated might be induced by the adsorption of dopants on the graphite surface.

To test the validity of this speculation, we have chosen adsorbed potassium atoms to act as charge donors. Our EELS results show that the surface plasmon frequency is indeed sensitive to small dosages of potassium. The observed increase of plasmon frequency can be interpreted in terms of a substantial electronic charge redistribution from the potassium adatom towards the graphite substrate.

2. Experimental procedure

The experiments were carried out in a UHV system with a routine pressure of 3×10^{-10} mbar. The specimen used was a piece of highly oriented pyrolitic graphite (HOPG) [2], which was cleaved in air and cleaned in vacuum by resistive heating to about 1100 K. Potassium was deposited by heating a SAES getter source which was mounted about 2 cm away from the specimen. The graphite substrate was kept at about 90 K in order to avoid intercalation of potassium atoms within the graphite

layers [3]. A single-pass hemispherical monochromator and analyser were used for both the EELS and low energy electron diffraction (LEED) measurements [4].

3. Results and discussion

EELS spectra obtained for three coverages of potassium on graphite are presented in figure 1 (left). An incident beam energy of 9 eV and an incident angle of 60° were used. One loss feature is observed in the EELS spectra, superimposed on the characteristic and intense graphite background caused by electron–hole pair excitations [5]. The frequency of this loss feature increases with the potassium coverage until it reaches a value around 320 meV; at higher coverages other loss excitations appear [6].

The corresponding LEED profiles are shown in figure 1 (right). At the lowest coverage, where the loss mode has a frequency of about 50 meV, a diffraction peak at a wavevector of 0.09 Å^{-1} can be clearly resolved†. If we take the coverage of the completed (2 × 2) close-packed phase, which is observed in the LEED measurements at higher coverages [6], to represent a full monolayer (1 ML), and assume that the low coverage structure has the hexagonal symmetry while it is being uniformly compressed as the coverage increases [7], we can derive the coverage from the wavevector of the
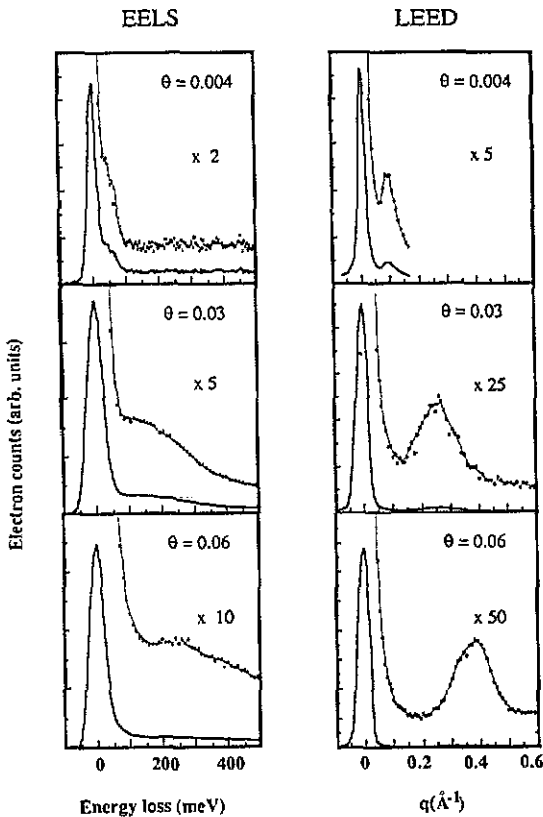
EELS   LEED

Figure 1. EELS spectra and LEED profiles for three coverages of potassium (θ_K) on graphite at 90 K. In each case the electron beam energy is 9 eV and the angle of inidence is 60° from the normal. In the top panel, where $\theta_K \approx$ 0.004 ML, the EELS was taken 2.5° away from the specular direction to enhance the loss feature against the background.

† Because of the azimuthally random distribution of microcrystalllites in HOPG, rings rather than spots are always obtained in conventional LEED measurements. Figure 1 thus represents a slice in one direction through the LEED ring; all diffraction features are sampled, but one cannot, for example, distinguish a solid phase from a highly correlated liquid.
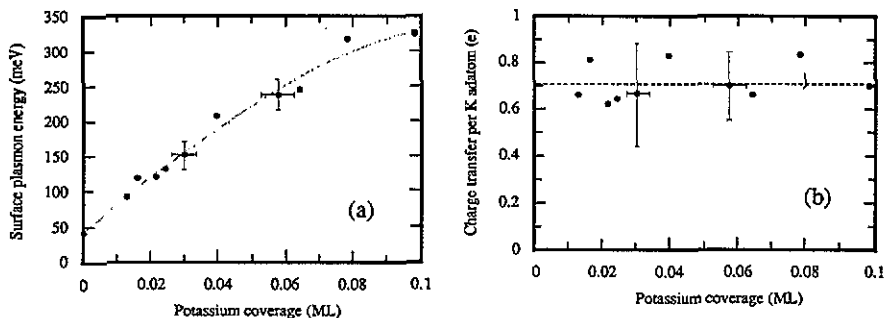
Figure 2. (*a*) Experimental plasmon frequency as a function of potassium coverage on graphite. (*b*) Charge transfer per potassium adatom, calculated from EELS and LEED data, as a function of potassium coverage.

diffraction peak induced by potassium. In figure 2(*a*), we have plotted the loss energy of the observed peak as a function of the potassium coverage obtained in this way for a number of spectra, of which those in figure 1 are examples. The loss energy is seen to rise monotonically as the coverage is increased. It is well known that the adsorption of alkali metal results in a decrease of the work function, yet the question of whether the change is due to charge transfer or to the polarization of adatoms still remains open. As we have pointed out in the introduction, the low density-of-states at the Fermi level of graphite suggests that the electronic excitation spectrum will be very sensitive to, and thus a signature of, a small change in the number of effective carriers and, thus to the redistribution of adatom charge towards the substrate.

The band structure calculation described by Jensen *et al* [1] allows one to determine the frequency of the plasmon mode as a function of the position of the Fermi level. As the Fermi level is either increased or decreased away from its position in the undoped graphite, where the minimum in the density of the states occurs, the plasmon frequency increases. In a clean graphite, the plasmon is not visible at 90 K, because (according to calculation) its frequency is too low at that temperature. The loss mode seen in figure 1 is consistent with the idea of a frequency shifted graphite plasmon, if we take it that the adsorption of potassium raises the effective carrier density for graphite, hence shifting the surface Fermi level upwards. Thus we assign the loss feature observed to a frequency shifted graphite surface plasmon.

It is of interest to estimate, within the framework of the classical point charge transfer model [8], the number of additional carriers in the graphite substrate arising from potassium adsorption, or, in other words, the amount of charge transfer per potassium adatom. In this framework we assume that the band structure of the graphite substrate is unperturbed by the adsorption of potassium; the Fermi level is merely shifted because of the charge transfer from the alkali. From the measured plasma frequency we first derive a Fermi level shift from the scheme of Jensen *et al* [1]. Then, using results obtained by Tatar and Rabii [9], who calculated the position of the graphite Fermi level as a function of the number of carriers added to the (bulk) material, we can convert the data for plasmon energy versus coverage in figure 2(*a*) to charge transfer per potassium adatom versus coverage. Since Tatar and Rabii's calculation applies to bulk graphite, we have to make a presumption about how the charge transfer from the alkali is distributed through the graphite substrate, and we assume that the transferred charge is confined to the topmost layer. In figure 2(*b*) we

show the graph derived according to this prescription. As we can see, the net effective charge transfer per potassium is around $0.7e$ for coverages below 0.1 ML. This is compatible with the value of $\approx 0.6e$ quoted for potassium adsorption on Ni(100) [10]. The almost constant value of the charge transfer as a function of coverage implies that the depolarization field arising from interaction between (polarised) potassium adatoms is negligible in this low coverage region.

It is important to stress that, in our derivation of the charge transfer, the assumption has been introduced that the band structure of graphite is unperturbed by the adsorbed alkali. Although the assumption has worked quite well in the case of intercalated graphite compounds [2], we do not wish to rule out the possibility that the plasmon mode observed is a global mode of the alkali-graphite system, e.g. where alkali oscillators are coupled together by the band structure of the substrate. In this case the band structure of the substrate would be perturbed by alkali adsorption, at least locally. At this stage we cannot probe the difference between charge transfer and charge redistribution. But we do think it is reasonable to conclude that, if what is happening is charge redistribution rather than charge transfer, the redistribution involves the graphite substrate in a significant way, and is not, for example, confined to the alkali monolayer.

We note finally that, as the K coverage is increased beyond 0.1 ML, the plasmon mode of figure 1 ceases to increase further in energy, and other excitation modes appear [6]. Simultaneously the close-packed 2×2 phase starts to grow. This implies that the frequency-shifted plasmon excitation is a characteristic of the potassium dispersed phase on graphite. This phase is likely to be a strongly correlated gas or low density fluid, while the other excitation modes are characteristic of the 2×2 solid phase. In summary we have reported the observation of an excitation mode in the potassium/graphite system, whose frequency shifts from about 50 to 320 meV, when the alkali coverage increases to 0.1 ML. The mode has been attributed to a perturbed graphite surface plasmon, with the support of a theoretical band structure calculation. We suggest that raising the potassium coverage increases the effective carrier density of the surface and with it the plasmon frequency. Within the framework of the rigid band model, we deduced that the charge transfer per potassium atom is about $0.7e$ and remains largely constant in the low coverage regime.

Acknowledgments

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