Helium Scattering from a Krypton Film on Graphite

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Scattering data are presented for a monoenergetic beam of ^{4}He incident on both commensurate and incommensurate Kr films adsorbed on graphite. For the commensurate layer, four bound-state resonance levels are observed, at binding energies 4.67, 1.86, 0.58, and 0.14 meV, which agree with a calculation incorporating three-body interactions. For the incommensurate layer, only the lowest level is identified; its binding energy of 5.2 meV also agrees with the calculation.

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Physically adsorbed films are intriguing and challenging because of the wide variety of phenomena they exhibit.[1-3] Atomic-beam scattering has emerged as an important contributor to this research, since it can reveal information about the surface structure and dynamics, as well as the interaction with the external atom.[3-7] This paper presents results to date on ^{4}He scattering by Kr films on graphite (Gr) in both the $\sqrt{3}\times\sqrt{3}$ commensurate (C) and the fully incommensurate (IC) structures. This problem is of particular interest because there exists an extensive body of thermodynamic data for He on Kr-plated graphite (including an ordering transition), for which the analysis requires knowledge of the interaction potential $V(r)$ between a He atom and the Kr/Gr solid.[2,8-10] The data presented here probe this interaction with a precision capable of assessing some subtle questions that arise in the theory. Some preliminary information concerning the nature of the C-IC transition[11-13] at the experimental temperature of about 50 K is also presented.

The ^{4}He beam used has an incident wave vector $k_i = 5.74 \pm 0.06$ Å^{-1}, an angular width of 0.03 deg, and a width of 0.4 mm at the crystal. The substrate samples are natural graphite crystals (Ticonderoga, N.Y.) about 3 mm in diameter and 0.5 mm thick, selected for flatness by optical microscopy and laser-beam reflection. The crystals are mounted with epoxy onto a small copper plug on a two-axis goniometer, thermally linked by copper braids to a Displex closed-cycle refrigerator. Prior to each experimental run the crystal is heated in the UHV chamber (base pressure 1×10^{-10} Torr) to about 900 K for about 1 h. The surface lattice constant can be measured with an absolute accuracy of $\lesssim 1\%$, the out-of-plane mosaicity of even the best crystals being the primary limiting factor. The temperature of the crystal mounting plug is measured by a platinum resistance thermometer and regulated to ± 0.1 K.

To deposit a film, the Kr gas (99.995% purity) is admitted through a UHV leak valve to a stainless-steel capillary aimed at the crystal. The rate of impingement corresponds to an equivalent pressure of roughly 10^{-8} Torr, resulting in a rise of the static background pressure in the chamber by about 2×10^{-10} Torr. As the deposition proceeds, the specular reflection intensity decreases quite linearly with time, then levels off after ~ 30 min. The crystal is then cooled from the deposition temperature of ~ 52 to ~ 45 K for the diffraction and bound-state resonance (BSR) measurements.[4] The latter are carried out by recording the specular intensity at fixed polar incidence angle θ while scanning the azimuthal angle ϕ. Figure 1 shows the results for the bare graphite and for several partial coverages obtained by interruption of the dosing. It is seen that the graphite pattern is gradually obscured and replaced by a new pattern characteristic of the overlayer. At the same time the $(\bar{1},0)$ diffracted peak from the overlayer grows in intensity. The coexistence of the bare-graphite and overlayer diffraction and BSR signals demonstrates that the Kr layer grows in an islandlike configuration. When the deposition is slow enough, the resulting lattice constant corresponds to the C-layer spacing, 4.26 Å. A sampling of a set of scans over a range of θ is shown in Fig. 2. In a BSR transition the particle is diffracted into a state where it is bound to the surface in the perpendicular direction but translating parallel to it. Kinematical relations, energy and quasimomentum conservation, restrict these transitions to certain loci in the plane of the parallel incident-wave-vector projection **K**. If the parallel translational motion is free-particle-like, the loci are circles centered at reciprocal lattice points of the surface mesh.[4,14,15] We interpret the intensity *minima* in Figs. 1 and 2 to be the BSR signatures for the following reasons: (1) Past experiments[14] and theoretical calculations[15] have shown that inelasticity in the scattering promotes the formation of minima at resonance, as is seen in Fig. 1 for the bare graphite, and the scattering from the Kr overlayer is indeed highly inelastic as evidenced by the strong decrease in specular intensity on dosing; (2) at the higher polar angles, where generally more resonances are kinematically allowed, there is a general diminution of the specular in-

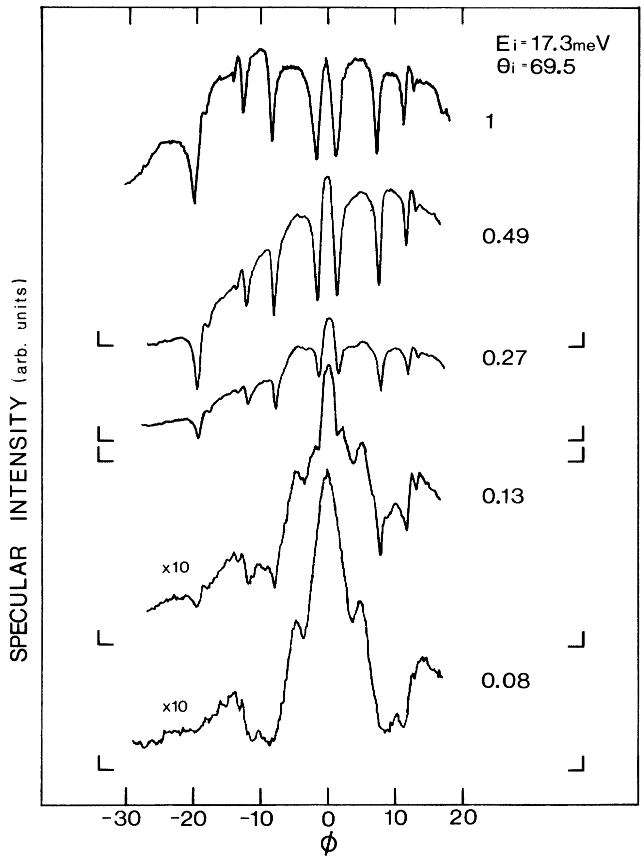

FIG. 1. Azimuthal scans of the specular intensity at a fixed polar angle, $\theta = 69.5°$, for various partial Kr dosings. The number at the right of each trace indicates the specular intensity at $\phi = 0$ (near-neighbor direction in overlayer) relative to the bare-graphite value (top curve).

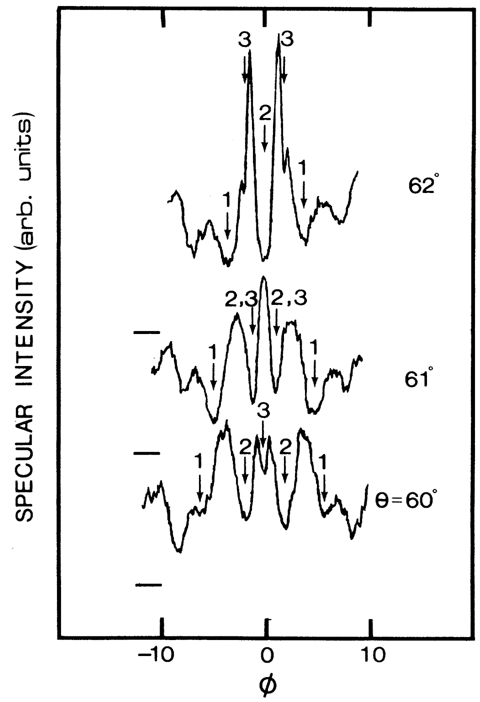

FIG. 2. Sample set of azimuthal scans of the specular intensity for an incident beam of ^{4}He with $k_i = 5.74$ Å^{-1} reflected from commensurate Kr/Gr. The arrows indicate the angular positions of the resonant minima for the (2,1) and $(\bar{2},\bar{1})$ resonances of the $n = 1$–3 levels.

tensity. The **K**-space positions of the minima are plotted in Fig. 3. Within the moderately large experimental uncertainty, many of these can be seen to lie on circles. The energy levels deduced from the radii are given in Table I below; the quoted uncertainties correspond to the deviations from circles.

IC films (compressed up to ~5% in lattice spacing) can be formed in two ways. With flow rates which produce a monolayer in 5–10 min, the film is IC immediately after deposition and cooling to ~40 K. Alternatively, an initially C film can be driven IC either by slowly increasing the Kr flow rate or by cooling under constant flow. In such cases, the C-IC transition was monitored by repeated scans of the overlayer $(\bar{1},0)$ diffraction peak. An intermediate phase in which the peak is weakened and broadened, followed by a resharpening in the shifted IC position, is observed. This is reminiscent of the behavior seen by x-ray diffraction[12] at higher temperatures and Kr pressures, but the weakening of the peak in our case is less

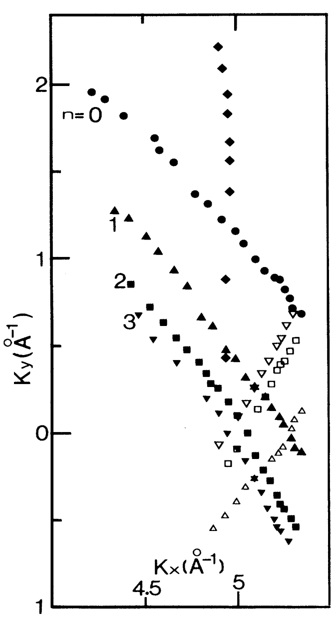

FIG. 3. Resonance values of parallel wave vector **K** for ^{4}He incident on commensurate Kr/Gr ($k_i = 5.74$ Å^{-1}). The labeled solid symbols indicate the (2,1) resonances and the corresponding open symbols the $(\bar{2},\bar{1})$. The unlabeled solid lozenges are for the $n = 2$, $(0,\bar{1})$ resonance.

drastic. Further studies of this transition are in progress.

Several sets of BSR scans were taken on IC layers prepared in both ways. Although the general appearance is quite similar to the C-layer scans, well-defined K-plane loci were obtained only for the lowest energy level, given in Table I. For the others, the patterns seem to be complicated by the presence of two orientations of rotated domains.[12,13]

For the theoretical analysis of these results, the interaction between a He atom and the Kr/Gr system is written[16]

$$V = V_2 + V_s + V_3^{g-a} + V_3^{g-s} + V_t. \qquad (1)$$

The largest term V_2 arises from the two-body interactions of the He atom with the Kr atoms on a triangular lattice $\{R_i\}$ in the plane $z=0$:

$$V_2(\mathbf{r}) = \sum_i U(|\mathbf{r}-\mathbf{R}_i|). \qquad (2)$$

The substrate contributes[17] additional two-body terms which can be summed to yield

$$V_s = -3C_3 d \sum_{n=0}^{\infty} (z+z_s+nd)^{-4}, \qquad (3)$$

where d is the separation between graphite layers and $C_3 = 180$ meV-Å^3 is the van der Waals coefficient[18] for He/graphite; the Kr distance above the graphite, $z_s = 3.3$ Å, is taken from LEED and surface extended x-ray-absorption fine-structure data.[19] The third and fourth terms of Eq. (2) arise from three-body interactions involving the He: V_3^{g-a} is a sum of the He-Kr-Kr interactions[20] in the form specified by Axilrod, Teller, and Muto (ATM)[21]; V_3^{g-s} includes the He atom, one Kr atom, and the substrate.[22] Finally, V_t is the thermal correction to V_2 associated with the Kr vibrations normal to the substrate.[23] As seen in Fig. 4, the successive terms in Eq. (1) are progressively smaller in magnitude. It is thus essential to estimate the leading terms accurately. Our two-body potential $U(x)$ is that of Watanabe, Allnatt, and Meath,[24] recently judged to be optimal on the basis of consistency with gas-phase experimental data.[25] An alternative He-Kr potential[26] yielded $\leq 1\%$ difference from our results discussed below.

We have numerically solved the Schrödinger equation for a ^{4}He atom in this potential. The lowest eigenvalues appear in Table I. They are observed to agree with the data within experimental error. We emphasize that there are no adjustable parameters in the calculation. The agreement thus suggests that the basic assumptions are correct. The most crucial of these are that $U(x)$ is not affected by proximity to the surface and that the ATM theory of three-body interactions[21] is applicable. The latter contributes 0.42 and 0.21 meV, respectively, to states $n=0$ and 1 for the C layer.

We note in passing that the same general approach has been applied to the case of He scattering from commensurate Xe/Gr.[16] There, the prediction is less certain because the He-Xe potential $U(x)$ is less well known. We find agreement with all three bound states observed by Bracco *et al.*[7] if the "MS"[26] version of $U(x)$ is employed. In contrast, the predicted resonance levels are 10% too shallow if the "HFD-1" potential[26] is used. This shows how surface scattering data can be used to distinguish between alternative pair potentials.[27]

To summarize, we have observed ^{4}He bound-state

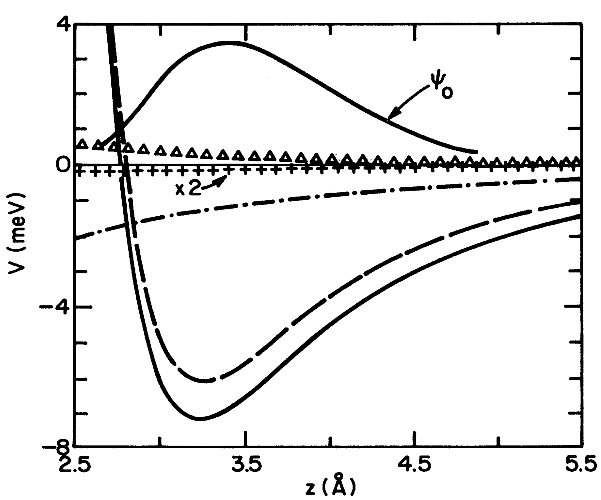

FIG. 4. Various contributions to the net interaction of a ^{4}He atom above a commensurate Kr layer on graphite. Solid curve is the net laterally averaged potential. Individual contributions are the two-body term V_2 (dashed line), the substrate term V_s (dash-dotted), V_3^{g-a} (triangles), and V_3^{g-s} (pluses). The thermal correction V_t, not shown, is ~ 0.05 meV near the minimum. The curve labeled ψ_0 is the ground-state wave function.

TABLE I. Binding energies E_n (in millielectronvolts) obtained from experiment, compared with theoretical values.

	C		IC[a]	
n	Theory[b]	Experiment	Theory[b]	Experiment
0	4.81	4.67 ± 0.14	5.18	5.2 ± 0.1
1	1.86	1.86 ± 0.15	2.09	. . .
2	0.61	0.58 ± 0.07	0.69	. . .
3	0.15	0.14 ± 0.04	0.17	. . .

[a]The IC coverage is 1.1 times the C coverage.

[b]Values shown were obtained from Eq. (1) with use of $U(x)$ given by Ref. 24 [called $U_b(D,k)$ there]. Results obtained with the alternative potential (Ref. 26) coincide except for $n=0$. In that case, $E_0 = 4.76$ meV for commensurate and 5.13 meV for incommensurate Kr/Gr.

resonances for both C and IC Kr/Gr. A theoretical study yields excellent agreement with the measured values, finding a nearly 10% contribution of three-body interactions. Predictions[16] of coverage dependence, band-structure effects, and ^{3}He resonances remain to be tested experimentally. Future extensions include a full scattering calculation to provide a more complete test of V, including its lateral variation.

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