Study of Gas-Graphite Potential by Means of Helium Atom Diffraction

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Scattering of thermal He atoms from a low-temperature graphite (0001) surface was carried out. The measured diffraction pattern shows that the repulsive part of the periodic gas-surface potential is rather well represented by the first Fourier component. The "hard wall" peak-to-peak spatial modulation is 0.21 Å. Bound-state resonances allow one to determine four distinct energy levels of the laterally averaged potential well. A comparison with available adsorption data is presented.

The exposed basal plane of graphite is of great value for the study of physisorption probelms because of its good uniformity and chemical inertness.[1] The development of high-quality graphite adsorbents (like Grafoil or Papiex) has recently aroused a renewed interest in these problems, particularly in connection with the occurrence of two-dimensional adsorbed phases and their interesting properties.[2]

A better and better knowledge of the graphite surface and its interaction with single atoms is required both for the interpretation of experimental results and for the development of the theory of physisorption. The diffraction of atomic beams from crystal surfaces is an ideal technique for obtaining information on the atom-surface interaction.[3] It has been used for a number of careful studies of alkali-halide, metal-oxide, and metal surfaces. In this paper we report the first scattering measurements carried out with a beam of He on a graphite (0001) surface.

The scattering apparatus has been described in previous papers.[4,5] The expanded supersonic beam had an average wave vector $k = 11.05$ Å^{-1}, with a full width at half-maximum (FWHM) spread of about 0.95 Å^{-1}. The graphite specimen was a natural single crystal,[6] having dimensions $5\times3\times0.3$ mm. The crystal was attached to the specimen holder by means of Aquadag and cleaved by exfoliation in air. The freshly cleaved surface was outgassed and annealed in high vacuum for several hours at 400°C. After lowering the temperature to 80 K in ultrahigh vacuum, scattered intensity measurements were carried out at different incident polar (θ_i) and azimuthal (φ_i) angles. The graphite surface lattice geometry is shown in the inset of Fig. 1, where the angle φ is also indicated.

A scan of the diffracted He intensity is shown in Fig. 1. Incoherent and inelastic background appears to be very small. The width of the specular peak is somewhat larger than that expected from the angular spread of the incident beam. This effect is due to irregularities of the surface which is actually made of a few adjacent twinned crystals having surface normals slightly misoriented: The effect can in fact become more pronounced for large incident angles or when the position of the incident beam is changed. Except for this, no other defect structure of the graphite crystal was observed. The diffraction peaks have the expected width and shape: From their angular location, measured under a variety of incident angles, a surface lattice parameter $a = 2.465 \pm 0.025$ Å is obtained, in good agreement with the

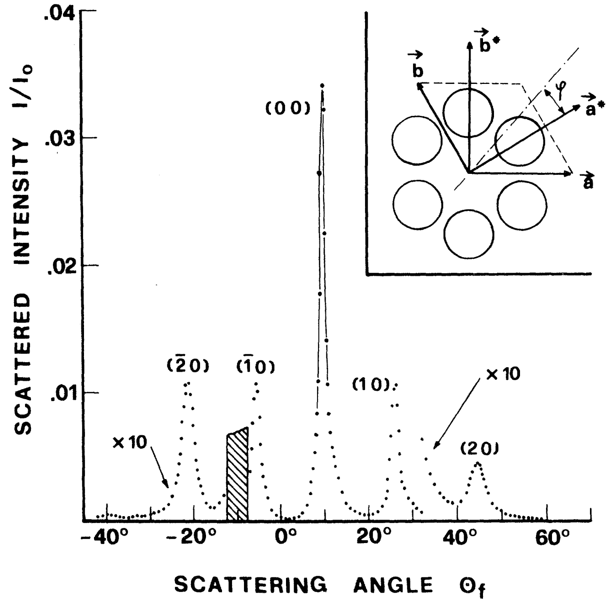

FIG. 1. In-plane scattered intensity, normalized to full beam intensity I_0, at $\varphi_i = 0°$, $\theta_i = 10°$. The second-order peaks are seen on a magnified scale. In the inset, the unit vectors of the direct and reciprocal surface lattice of graphite (0001) are shown. The circles represent carbon atoms.

bulk value.

From the diffraction patterns obtained for in-plane scattering at a few different θ_i, with φ_i equal to 0 and 30°. diffraction probabilities were derived by using the procedure described in a previous paper.[4] By carrying out intensity measurements of the specular beam as a function of φ_i or θ_i, sharp bound-state resonances were observed, as shown by the examples given in Fig. 2. We recall that resonances occur when a virtual diffraction channel $\vec{B}$ is open, for which $k^2 - (\vec{K}+\vec{B})^2$ approaches the values $2m\epsilon_j/\hbar^2 < 0$. Here $\vec{k}(\vec{K}, k_z)$ is the incident wave vector, $\vec{B}$ is a surface-reciprocal-lattice vector, m is the helium mass, and ϵ_j are the energy levels of the laterally averaged gas-surface potential well. More precisely, when the two quantities given above become equal, minima are usually observed in the specular intensity. The observed minima correspond to different $\vec{B}$ vectors and to four levels with energy $\epsilon_0 = -11.7 \pm 0.3$ meV, $\epsilon_1 = -6.1 \pm 0.4$ meV, $\epsilon_2 = -2.6 \pm 0.3$ meV, and $\epsilon_3 = -0.9 \pm 0.2$ meV (-136, -71, -30, and -10.5 K, respectively). No other bound state above ϵ_3 is seen; however, a shallow structure corresponding to $k^2 - (\vec{K}+\vec{B})^2 = 0$ seems to be present, indicating the occurrence of a threshold surface resonance.

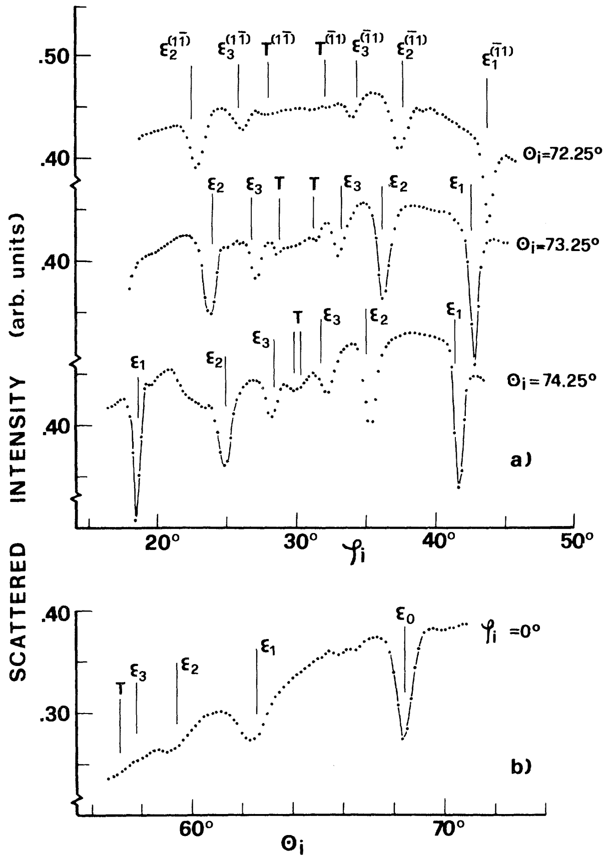

FIG. 2. Specularly scattered intensity (a) as a function of φ_i at different θ_i values and (b) as a function of θ_i at $\varphi_i = 0°$. The angular positions for which the resonance condition is satisfied are shown by the bars. They correspond to the energy levels given in the text. T indicates the location of the threshold. The minina shown in (a) are related to resonances involving a $\vec{B}$ vector labeled $(1\bar{1})$ or $(\bar{1}1)$; the minima in (b) are related to both (01) and $(1\bar{1})$ $\vec{B}$ vectors.

In order to interpret the intensity distribution among different diffraction peaks the corrugated hard-wall model with a well has been used[7]: This theoretical model has proved to be a very good approximation for strongly repulsive gas-surface potentials like the one present in our case.[8] Using the eikonal approximation, furthermore, the elastic diffraction probability for the $\vec{G}$ peak is given by

$$P_G = \frac{\cos\theta_G}{\cos\theta_i}\frac{1}{A^2} \times \left| \int_{\mathrm{u.c.}} \exp i[\vec{G}\cdot\vec{R} - q_{Gz}'\zeta(\vec{R})]\, d^3R \right|^2, \quad (1)$$

where the integration is performed over the unit cell of area A and $q_{Gz}' = k_i[(\cos^2\theta_i + D/E)^{1/2} + (\cos^2\theta_G + D/E)^{1/2}]$, D and E being the average well depth and the incident energy, respectively. The shape function $\zeta(\vec{R})$ was assumed to be equal to

$$2\zeta_{10}\{\cos(2\pi x/a) + \cos(2\pi y/a) + \cos[2\pi(x-y)/a]\},$$

which is the first Fourier component of the expansion $\zeta(\vec{R}) = \sum_G \zeta_G \exp(i\vec{G}\cdot\vec{R})$, x and y being oblique coordinates in the direction of unit lattice vectors $\vec{a}$ and $\vec{b}$, respectively.

Taking $D \simeq 15$ meV, as derived from the bound-state levels, expression (1) was numerically integrated and the parameter ζ_{10} was evaluated from a best fit to the relative experimental diffraction probabilities. Only data relative to small θ_i and θ_G were considered in order to minimize multiple-scattering effects, which are not taken into account by Eq. (1). The agreement between theoretical and experimental probabilities is satisfactory; they differ by a common factor of about 0.24, which is a measure of the Debye-Waller factor $\exp(-2W)$. ζ_{10} is evaluated to be -0.023 ± 0.002 Å, which corresponds to a peak-to-peak spatial modulation of the "hard wall" of about 0.21 Å.[9] No serious attempt to include higher Fourier components was made, but a qualitative evaluation shows that they are much smaller than the first one.

The spectrum of bound states allows us to give an evaluation of the attractive part of the helium-graphite potential; the measured ϵ_j's are in fact the eigenvalues of $v_0(z) = (1/A)\int_{\text{u.c.}} v(\vec{\text{R}}, z) d^3R$, $v(\vec{\text{R}}, z)$ being the full three-dimensional gas-surface potential. Neither a Morse potential, nor a 3-9 potential[10] is able to represent accurately the experimental spectrum. A well depth ranging from 170 to 190 K is found. It is puzzling that a fifth level expected around 2.5 K is not seen in the experimental data.

A detailed calculation of the rare-gas–graphite (0001) interaction was carried out by Steele[11] with the assumption that $v(\vec{\text{R}}, z)$ is the sum of semiempirical pairwise potentials. Steele points out that $v(\vec{\text{R}}, z)$ is sufficiently well approximated by taking into account only the zero- and first-order Fourier component and finds that only the repulsive part of the potential is appreciably modulated by the surface periodicity. This is in agreement with our findings; however Steele's first Fourier component of the repulsive potential is roughly $\frac{2}{3}$ of what we find experimentally and his potential well is too deep. The same observations can be made concerning the He-graphite potential used by Giamello *et al.*[12] These semiempirical potentials were the basis for the band-structure calculations of He adsorbed on graphite carried out by Hagen, Novaco, and Milford[13] and by Giamello *et al.*[12] Although the real potential has a slightly larger periodicity strength, the calculated bandwidth should not be remarkably affected. We would like to note that the present scattering data do not give direct information on the height of the potential barriers opposing surface migration,[14] a problem of great interest in adsorption kinetics and thermodynamics.

Finally, we compare the present results with the information gathered by means of adsorption experiments on exfoliated graphite. Calorimetric and vapor pressure studies of He on Grafoil in the temperature range 4–15 K were carried out by Elgin and Goodstein.[15] These authors were able not only to derive a quite accurate value for the binding energy of a single atom—amounting to $E_0 = -143 \pm 2$ K—but also to evaluate the energy of the first excited vibrational state, $E_1 = -89 \pm 3$ K. The first value compares well with our ϵ_0, the second stays lower than ϵ_1, likely because of band-structure effects.[12,13] Lerner and Daunt[16] derive the He binding energy by extrapolating the isosteric heat of adsorption in the limit of zero coverage; they give E_0 ranging from 105 to 155 K, in agreement with our result.

In conclusion, we hope that the present data, as others obtainable from scattering, may contribute to the assessment of some of the open questions pertaining to physisorption problems.

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