PHYSICAL REVIEW B VOLUME 24, NUMBER 4 15 AUGUST 1981

Diffractive scattering of H atoms from an ordered xenon overlayer adsorbed on the (0001) surface of graphite

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(Received 15 June 1981)

H-atom diffractive scattering was carried out from a $\sqrt{3}\times\sqrt{3}$ lattice of xenon atoms adsorbed on the (0001) surface of graphite. The experimental data are well reproduced by a hard-wall scattering model, both with and without a correction due to the attractive part of the potential, resulting in peak-to-peak corrugations of 1.07 ± 0.05 and 1.19 ± 0.05 Å, respectively. A realistic H-Xe-C(0001) potential, based on the assumption of pairwise additive atom-adatom interactions, is calculated and found to have a corrugation of 0.99 ± 0.05 Å.

During the last few years, there has been a great deal of activity devoted to the study of two-dimensional phases of molecular layers adsorbed on solid surfaces[1] with the aim of improving our knowledge of (a) phase transitions in two-dimensional systems, (b) thermal desorption phenomena, and (c) the lattice dynamics of adsorbed layers. These properties have been widely studied using different techniques such as ellipsometry, x-ray diffraction, Mössbauer spectroscopy, heat-capacity measurements, and neutron diffraction.[2] However, all these methods require a large volume of adsorbate, and are therefore restricted to the study of exfoliated graphite (e.g., Grafoil) which does not have a well-defined microscopic structure. Up to now only LEED (low-energy electron diffraction) and THEED (transmission high-energy electron diffraction) have been successfully used in studying molecular adsorbates on single-crystal surfaces. By measuring in fact the position of the LEED spots due to the overlayer as a function of both pressure and temperature, the phase diagram of the adsorbate was accurately determined in the case of noble gases on the (0001) graphite face[3,4] and of xenon on the NaCl (001)[5] and copper (100) surfaces.[6] Atomic-beam diffraction experiments from molecular layers adsorbed on single crystals recommend themselves not only because of their obvious complementarity with LEED experiments, but also because they offer some advantages such as an increased surface coverage sensitivity and a lack of layer penetration. Furthermore, this is the only method for studying directly the atom-layer potential by carrying out both diffraction-probability and selective-adsorption measurements. Finally, time-resolved atomic-beam diffraction can be used in studying the dynamics of the absorbed layer. Although there is obvious interest in the method, the only experiments in this direction have been the preliminary studies of Mason and Williams[7] on water, ethanol, and CCl_4 adsorbed on the NaF(001) surface probed by a He beam and those carried out by Rieder and Engel[8] which involve metal substrates and strong chemisorptive bonding between the solid and the adsorbed layer.

In this Communication we present the first results of diffractive scattering of H atoms at thermal energies from a xenon overlayer adsorbed on the basal plane of natural graphite. The importance of the work resides not only in showing the capability of the atomic diffractive scattering technique to study two-dimensional phases, but also in the fact that for the H-Xe system the two-body potential is quite well known[9] so that it is possible to construct a realistic gas-surface potential to be compared with the experiment.

The experimental setup is the same used in several atom-surface scattering experiments[10–12] recently performed in our laboratory. It consists of a H beam of good angular (0.8°) and momentum [14% FWHM (full width at half maximum)] resolution, which is detected by a rotatable high-sensitivity bolometer. In the present experiment, in order to grow the xenon layer, an additional source of xenon atoms has been introduced into the chamber containing the crystal holder. The xenon gas used had a minimum purity of 99.995%, while particular care was taken in order to minimize the outgassing of the gas handling system. The sample, which is kept in poor thermal contact with a liquid-helium cryostat, can be varied in temperature from 15 to 600 K, by regulating the current flowing through a tungsten strip located behind it. The sample temperature was measured by means of a thermocouple in good thermal contact with it, stablized by an electronic feedback between the temperature reading and the input power of the heater. With this arrangement the crystal temperature during the scattering experiment can be determined within 10% below 30 K and within 1% or better in the high-temperature region. The single crystal of graphite used[13] was cleaved in air by exfoliation and outgassed in UHV for several hours at 550 K.

The (0001) graphite surface is first characterized by measuring the (10) and $(\bar{1}0)$ diffraction peaks along the $\phi = 0$ azimuth.[14] The (20) and $(\bar{2}0)$ peaks and the (21) and $(\bar{2}\bar{1})$ peaks along the $\phi = 30°$ azimuth, although kinematically allowed, are not observed because, due to the rather weak corrugation of graphite,[12] they have very small intensities. After the surface characterization, the xenon beam ($10^{15 \pm 1}$ mol $\mathrm{cm}^{-2}\,\mathrm{sec}^{-1}$ at the graphite surface) is switched on and the temperature of the surface is decreased from the initial value of 80 K, continuously monitoring the intensity of the specular peak. When the surface temperature reaches 69 ± 1 K, the specular peak sharply decreases, the xenon flux is interrupted and the surface temperature is reduced to 26 ± 3 K. Under these conditions we measured the diffraction patterns shown in Fig. 1 for three different azimuthal directions and for an incidence angle $\theta_i = 1.7° \pm 0.3°$. Several new peaks are now easily resolved and their angular positions clearly identify a $\sqrt{3} \times \sqrt{3}$ structure with the xenon atoms occupying the center of every third graphite hexagon. The wide nonsymmetric background, which is also observed with the (0001) graphite surface,[15] is due at least in part to irregularities in the natural graphite crystal.

A quantitative determination of the lattice parameter D of the xenon overlayer has been carried out using the following procedure: The diffraction pattern of the clean graphite was first fitted[14] using a lattice parameter d of 2.465 Å in order to determine the average value of the incident wave vector $\bar{K} = 6.45 \pm 0.07$ Å^{-1}; subsequently, using this $\bar{K}$ value, the angular positions of the diffraction peaks of the xenon overlayer were fitted using D as a free parameter, by means of the procedure described in Ref. 10. We obtained $D = 4.26 \pm 0.05$ Å which corresponds within the experimental errors to a structure in registery with the substrate.

The diffraction intensities were interpreted using the hard-wall model and the eikonal approximation of Garibaldi *et al.*[16] In this context the elastic diffraction probability for an incident waver vector $\vec{k}_i$ and $\vec{G}(m,n)$ peak, has the form

$$P_{\vec{G}} = \frac{\cos\theta_G}{\cos\theta_i} \left| \frac{1}{A} \int_{\mathrm{uc}} \exp[iq_{\vec{G}z}\xi(\vec{R}) + i\vec{G}\cdot\vec{R}]\,d^2\vec{R} \right|^2 , \tag{1}$$

where A is the area of the unit cell (uc) and $\hbar q_{\vec{G}z}$ is the transferred momentum given by

$$q_{\vec{G}z} = k_i[(\cos^2\theta_i + \epsilon/E)^{1/2} + (\cos^2\theta_G + \epsilon/E)^{1/2}] . \tag{2}$$

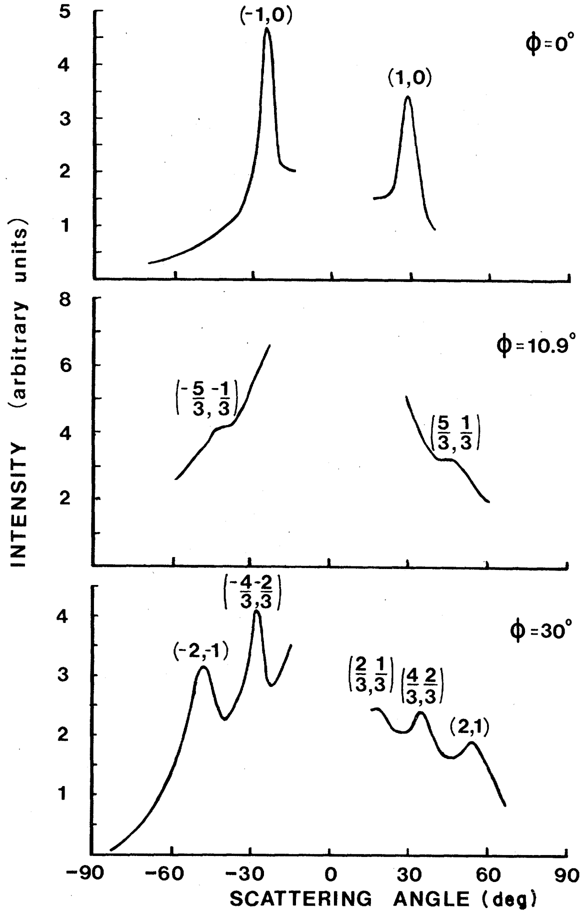

FIG. 1. H-atom scattering from the $\sqrt{3} \times \sqrt{3}$ xenon overlayer in registry with the C(0001) substrate. Patterns for three different values of the azimuthal angle ϕ are shown. The indices and ϕ refer to the graphite reciprocal lattice vectors. $\theta_i = 1.7° \pm 0.3°$; substrate temperature is equal to 26 ± 3 K.

Here E and ϵ are, respectively, the energy of the incident beam (1000 K) and the well depth of the laterally averaged potential. $\vec{R} \equiv (x,y)$ is the vector on the surface, (x,y) the oblique coordinates in the direction of the surface unit lattice vectors, and $\xi(\vec{R})$ the shape function of the surface, which in our case was assumed to be

$$\xi(\vec{R}) = 2\xi_{10} \left(\cos\frac{2\pi x}{D} + \cos\frac{2\pi y}{D} + \cos\frac{2\pi(x+y)}{D} \right) . \tag{3}$$

The elastic scattering probability of each peak was determined from the angular intensity distributions following the procedure of Ref. 10. The results depend on the estimation, done by eye, of the incoherent background due to (a) irregularities of the substrate, (b) defects in the xenon layer, and (c) inelastic scattering. However, since the results were found to be independent from the person doing the above-mentioned estimate, it was possible to carry out the analysis, comparing *relative* diffraction probabilities, by simply scaling the probabilities calculated with Eq. (1), using a numerical integration with the scaling factor and ξ_{10} as free parameters. Assuming for the H-atom–surface well depth ϵ the value of 220 ± 10 K, as explained below, we have determined ξ_{10} to be 0.119 ± 0.005 Å which corresponds to a peak-to-peak corrugation of 1.07 ± 0.05 Å. If the correction due to the attractive part of the potential is left out, the peak-to-peak corrugation becomes 1.19 ± 0.05 Å. The error is the statistical one and does not include, of course, systematic uncertainties due to the procedure discussed above.

In analogy with what has been recently done by Steele[17] and Levi *et al.*[18] for other systems, we compared the corrugated wall model results to the isopotential surfaces of the H–Xe-C(0001) interaction $V(\vec{R},z)$ which is assumed to be

$$V(\vec{R},z) = \sum_j V(r_j) \frac{-C_3}{(z+Z_0-\frac{1}{2}c)^3} \ , \tag{4}$$

where $V(r_j)$ is the H-Xe pairwise potential with r_j the distance between the impinging H atom and the jth atom of the xenon layer. The last term in the right-hand side of Eq. (4) is an attractive contribution due to the long-range interaction between the H atom and the graphite substrate with $C_3 = (4.60 \pm 0.07) \times 10^3$ K Å^3 as calculated by Vidali *et al.*,[19] with the Xe-C(0001) surface distance Z_0 equal to 3.5 Å (as estimated from the Ar-C(0001) and Kr-C(0001) results of Ref. 20(a) and with c representing the interplanar graphite distance Ref. 20(b). The $V(r_j)$ H-Xe pairwise potential is described through a combination of short-range repulsion and semiempirical long-range calculations, as has been shown by Ahlrichs *et al.*[21] and Tang and Toennies.[22] The model has been recently improved by Douketis *et al.*[23] assuming that $V(r_j)$ has the following form:

$$V(r_j) = A r_j^{\beta} e^{-\alpha r_j} - \left| \sum_n C_n r_j^{-n} g_n(\rho r_j) \right| f(\rho r_j) \ , \tag{5}$$

$$n = 6, 8, 10, 12, 14 \ ,$$

where the values of the coefficients A, β, α, C_n and of the damping functions $g_n(r_j)$ and $f(r_j)$ are reported in Table I. The C_n coefficients are those of Tang *et al.*[24]; the $g_n(r_j)$ functions correct the dispersion terms for charge overlap effects and $f(r_j)$ takes into account the corrections to the dispersion interaction for exchange overlap and higher-order effects. A, β, and α have been obtained by fitting Eq. (5) to the H-Xe potential experimentally determined via integral cross-section scattering measurements.[25] For the incident energy of the H atoms used in the present experiment, the maximum difference between classical turning points of the computed $V(\vec{R},z)$, $\Delta z = 0.99 \pm 0.05$ Å, is in agreement with the peak-to-peak corrugations reported above. The agreement confirms the model assumed for the H–Xe-C(0001) interaction, but a more accurate comparison should be made

TABLE I. H–Xe-C(0001) potential parameters.

A	640.9	hartree bohr$^{-\beta}$
β	0.3242	. . .
α	2.219	bohr^{-1}
C_6	40.9	hartree bohr^6
C_8	927	hartree bohr^8
C_{10}	2.546×10^4	hartree bohr^{10}
C_{12}	8.711×10^5	hartree bohr^{12}
C_{14}	3.620×10^7	hartree bohr^{14}
ρ	0.962	. . .
$f(\rho r) = 1 - (\rho r)^{1.68} \exp(-0.78 \rho r)$		
$g_n(\rho r) = \{1 - \exp[-2.1 \rho r/n - 0.109(\rho r)^2/\sqrt{n}\,]\}^n$		
where r is the H-Xe distance in bohr		
C_3	9.85×10^{-2}	hartree bohr^3
Z_0	6.6	bohr
c	6.33	bohr

by calculating the diffraction probabilities using $V(\vec{R},z)$ as given by Eq. (5). This may also shed some further light on the several different approximate theories available for the calculation of diffracted intensities.

In summary we have shown the potential of atomic-beam scattering for the study of two-dimensionally ordered structures. We have reported the first measurements of the diffraction of H atoms from a $\sqrt{3}\times\sqrt{3}$ xenon layer in registry with a graphite (0001) substrate. Furthermore a realistic model of the H–Xe-C(0001) interaction obtained by generalizing a hybrid Hartree-Fock plus damped dispersion theoretical model of Douketis *et al.*[23] is reported and good agreement with the experimental results is found. This clearly indicates that the same model can be used in predicting the interaction for other systems.

ACKNOWLEDGMENTS

It is a pleasure to thank G. Dorbolo for his help in calculating the H–Xe-C potential. Thanks are also due P. Rowntree for his help during the experiments and the staff of the Science Shop for their able cooperation. We are grateful to Professor L. Bruch for a useful discussion on the theoretical H-surface potential.

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[1] See, for example, *Ordering in Two Dimensions,* edited by S. K. Sinha (North-Holland, Amsterdam, 1980); and *Phase Transitions in Surface Films,* edited by J. G. Dash and J. Ruvalds (Plenum, New York, 1981).

[2] See, for example, J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975); W. A. Steele, *The Interaction of Gases with Solid Surfaces* (Pergamon, Oxford, 1974); J. Phys. (Paris) 38, C4-1 (1977).

[3] J. Suzanne, J. P. Coulomb, and M. Bienfait, Surf. Sci. 40, 414 (1973); B. Mutaftschiev, *ibid.* 61, 93 (1976); M. Bienfait and J. A. Venables, *ibid.* 64, 425 (1977); C. G. Shaw and S. C. Fain, Jr., 83, 1 (1979).

[4] J. A. Venables, H. M. Kramer, and G. L. Price, Surf. Sci. 55, 373 (1976); 57, 782 (1976); J. A. Venables and P. S. Schabes-Retchkiman, *ibid.* 71, 27 (1978).

[5] A. Glachant, J. P. Coulomb, and J. P. Biberian, Surf. Sci. 59, 619 (1976).

[6] A. Glachant and U. Bardi, Surf. Sci. 87, 187 (1979).

[7] B. F. Mason and B. R. Williams, Surf. Sci. 45, 141 (1974).

[8] K. H. Rieder and T. Engel, Phys. Rev. Lett. 43, 373 (1979).

[9] J. P. Toennies, W. Welz, and G. Wolf, J. Chem. Phys. 87, 614 (1979).

[10] G. Caracciolo, S. Iannotta, G. Scoles, and U. Valbusa, J. Chem. Phys. 72, 4491 (1980).

[11] S. Iannotta and U. Valbusa, Surf. Sci. 100, 28 (1980).

[12] T. H. Ellis, S. Iannotta, G. Scoles, and U. Valbusa, J. Vac. Sci. Technol. (in press).

[13] The single graphite crystal has been obtained by dissolving marble rocks from the Essex County (N.Y.) purchased from Ward's Natural Science Establishment Inc., Rochester, N.Y.

[14] For the graphite lattice convention, see H. Chow, Surf. Sci. 79, 157 (1979).

[15] See also E. Ghio, L. Mattera, C. Salvo, F. Tommasini, and U. Valbusa, J. Chem. Phys. 73, 556 (1980).

[16] U. Garibaldi, A. C. Levi, R. Spadacini, and G. Tommei, Surf. Sci. 48, 669 (1975).

[17] W. A. Steele, Surf. Sci. 97, 478 (1980).

[18] A. C. Levi, R. Spadacini, and G. E. Tommei, Surf. Sci. (in press).

[19] G. Vidali, M. W. Cole, and G. Schwartz, Surf. Sci. 87, 1273 (1979).

[20] (a) C. G. Shaw, S. C. Fain, Jr., M. D. Chinn, and M. F. Toney, Surf. Sci. 97, 128 (1980); (b) E. Zaremba and W. Kohn, Phys. Rev. B 13, 2270 (1976).

[21] R. Ahlrichs, R. Penco, and G. Scoles, Chem. Phys. 19, 119 (1977).

[22] K. T. Tang and P. Toennies, J. Chem. Phys. 66, 1486 (1977).

[23] C. Douketis, G. Scoles, S. Marchetti, M. Zen, A. J. Takkar, J. Chem. Phys. (in press).

[24] K. T. Tang, J. M. Norbeck, and P. R. Certain, J. Chem. Phys. 64, 3063 (1976).

[25] J. P. Toennies, W. Welz, and G. Wolf, J. Chem. Phys. 71, 614 (1979).