Observation of Orientational Ordering of Incommensurate Argon Monolayers on Graphite

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The relative orientation between solid argon monolayers and the basal plane of graphite single-crystal substrates has been measured as a function of mean overlayer interatomic spacing d by low-energy electron diffraction for $32\ \mathrm{K} \lesssim T \lesssim 52\ \mathrm{K}$. For $3.82\ \text{Å} \lesssim d \lesssim 3.95\ \text{Å}$, the measured orientation varies with d as quantitatively predicted by Novaco and McTague because of periodic static distortions of the argon monolayers by lateral argon-graphite forces. The relevance of these results to Villain's calculations is discussed.

Direct evidence for rotation of a physically adsorbed overlayer caused by the very weak lateral variation in adsorption energy along a graphite basal-plane substrate is presented for the first time. The angular orientation of a solid Ar monolayer with respect to the graphite substrate varies significantly with the mean interatomic spacing, which is changed by varying the Ar gas pressure and the substrate temperature. The precision of our low-energy electron-diffraction (LEED) measurements permits a direct comparison with predictions of Novaco and McTague (NM), who have developed a theory incorporating substrate-induced modulations of overlayer atom positions.[1,2] We find good agreement over a relatively wide range of Ar lattice constants and offer plausible reasons for a deviation at smaller distances. In addition to testing the theory for Ar, our measurements imply a low defect concentration in single-crystal graphite substrates used in other adsorption studies,[3,4] allowing the application of recent theory[5] to those experiments.

The adsorption energy of heavy inert-gas atoms (Ar, Kr, Xe) on the graphite basal plane varies by only a few percent within a graphite unit cell.[6] When the interatomic spacing d in an adsorbed solid monolayer (such as Kr or Xe) is sufficiently close to that of a structure commensurate with the graphite surface, such as the $(\sqrt{3}\times\sqrt{3})30°$ structure ($d = 4.26$ Å), the lateral adatom-substrate forces due to this small variation in adsorption energy produce noticeable effects in the structure and thermodynamics of the adsorbed phase.[3,7] Even for a solid Ar monolayer with d about 10% different from that of the $(\sqrt{3}\times\sqrt{3})30°$ structure, NM predicted that the lateral variation in adsorption energy still exerts an observable effect on the monolayer.

In their theory of static distortion waves, NM were able to show that the substrate causes a mean variation in the position of the jth overlayer atom from its lattice site $\vec{R}_j$, given by $\langle\vec{u}_j\rangle = \sum_G \vec{A}_G \sin[\vec{G}\cdot(\vec{R}_j-\vec{\Delta})]$, where $\vec{G}$ is a substrate reciprocal lattice vector, $\vec{\Delta}$ locates a center of inversion symmetry for the gas overlayer, and $\vec{A}_G$ depends on the ratio of lateral adatom-substrate force to adatom-adatom force in the Gth Fourier component. In addition, NM showed that in some situations these static distortion waves would minimize the total energy of the system if the overlayer were rotated from the orientation of a $(\sqrt{3}\times\sqrt{3})30°$ structure by an angle θ that is generally not a symmetry angle of the system. The combination of rotation and distortion would allow the atoms to approach the lowest-energy adsorption sites slightly without undue strain in the lattice. From approximate Ar-Ar and Ar-graphite potentials,[6] NM were able to compute the minimum-energy angle θ for a range of Ar nearest-neighbor distances.[2] We present below quantitative LEED measurements of θ and d that in general agree with these predictions.

The LEED apparatus was the same as previously described,[3,8,9] except that a 60-K cold surface was installed in the vacuum chamber to prevent contamination of the graphite surface with methane during argon exposure. Methane background pressure would otherwise increase at a constant rate while the ion pumps were turned off when admitting argon. In addition to decomposing under the primary electron beam and producing a disordered substrate surface, we found that methane impurities significantly affect the argon overlayer parameters θ and d.[10]

Under the conditions of our experiment electron-beam desorption effects on the adsorbed Ar layers were found to be insignificant, in marked contrast to earlier studies of thick Ar films on Nb(100).[11] Thus LEED is an ideal technique to search for small changes in rotational orientation between substrate and overlayer, as compared, for example, to neutron diffraction,[12] where the low surface sensitivity requires samples of large specific area. The large area is usually obtained by using exfoliated graphite, which is made up of many crystallites with random azimuthal orientation, so that diffraction occurs in rings rather than spots, masking any orientational epitaxy of the overlayer.

Figure 1 is a schematic drawing of the two-dimensional reciprocal lattice vectors expected for two oppositely rotated groups of Ar atoms for one set of (θ, d) predicted by NM.[1] Multiple scattering through first-order diffraction by the graphite and subsequent first-order diffraction by the overlayer is also shown. The schematic corresponds to what is actually seen in LEED patterns (Fig. 2). The multiple-scattering spots were quite evident at certain primary electron energies, and permitted substantial improvement in precision if taken into account when extracting the Ar lattice constant d from the pattern. Most measurements were made at a primary energy E_p = 58 eV, with a current of $I_p \approx 3$ nA and beam size of about 0.5 mm diam. Substrate temperatures were in the range 32 K $\lesssim T \lesssim$52 K and argon gas pressures ranged from about 10^{-8} to 10^{-4} Torr.

In Fig. 3 representative experimental data are shown along with the theoretical θ-vs-d line from NM.[2] It can be seen that the data at a given d are relatively insensitive to temperature. To within the error bars (calculated from the standard error in measuring θ and d), the agreement between experiment and theory is very good for the larger d, considering that the calculation[1,2] used T = 0 harmonic theory, approximate potentials, and linear response of the overlayer atoms to the substrate potential. (NM will present a detailed discussion of their calculations elsewhere.[13]) The deviation observed for $d \lesssim 3.82$ Å may be due to an increased number of second-layer atoms at the lower T and higher P required to produce the smaller d, or to edge interactions of the different groups of Ar atoms on the surface.

The modulations of the Ar atoms from their lattice sites will in principle produce LEED satellites,[2,3] some in the same place as the multiple-scattering spots. As yet we have not seen these satellites, which would be other evidence of the static distortion waves. The satellites will be even less evident in Ar than in systems closer to registry such as Kr or Xe where the satellites are expected to be more intense, but have not yet been seen. In Kr and Xe these modulations do produce observable effects on the thermodynamics of the monolayer.[3,7]

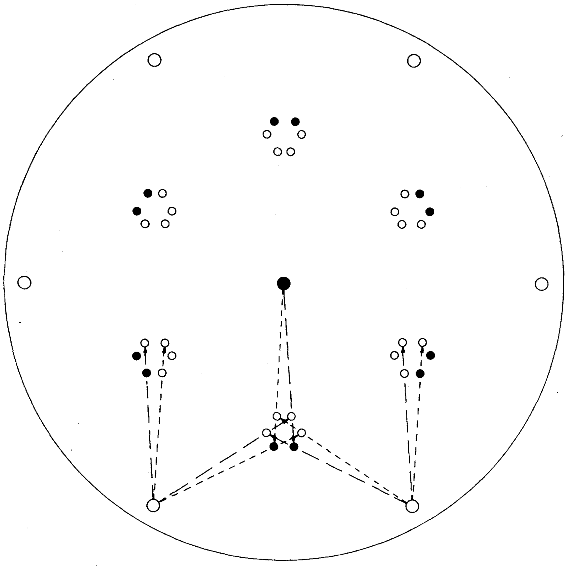

FIG. 1. Schematic LEED pattern for Ar overlayer with two oppositely rotated groups of Ar atoms having mean nearest-neighbor distance d =3.86 Å and orientations $\theta = \pm 3.5°$ (θ and d of Ref. 1). Diffraction beams represented are the specular (center closed circle), first-order graphite (peripheral open circles), first-order Ar (twelve closed circles), and graphite plus Ar (remaining 24 open circles). Some of the argon reciprocal-lattice vectors are shown as dashed lines (long dashes for $\theta = +3.5°$, short dashes for $\theta = -3.5°$).

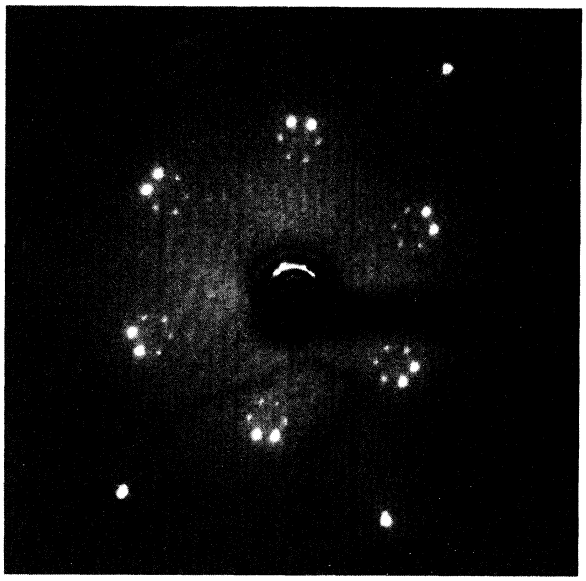

FIG. 2. Photograph of LEED pattern at 133 eV, 39 K, and 5×10^{-7} Torr Ar pressure. Three of the six first-order graphite diffraction beams are visible at the edge of the pattern; the remaining 36 spots result from the Ar solid monolayer as explained in Fig. 1. d =3.83 ±0.01 Å and $\theta = 3.55° \pm 0.15°$.

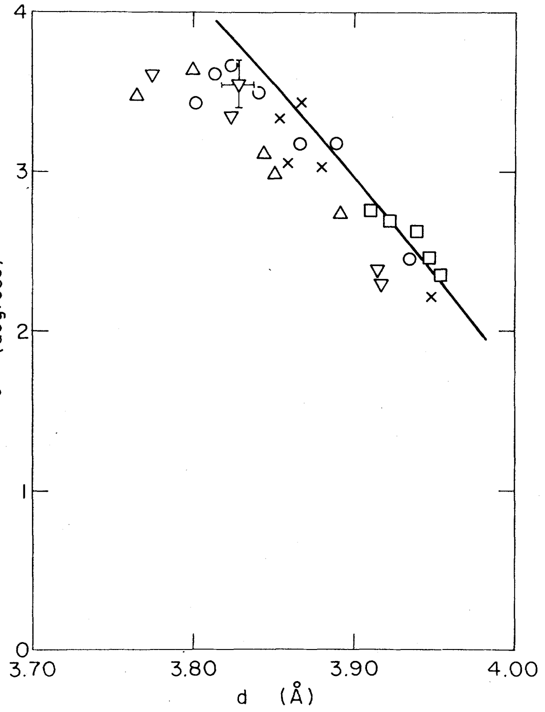

FIG. 3. Relative orientation θ between Ar monolayers and a $(\sqrt{3}\times\sqrt{3})30°$ structure ($d = 4.26$ Å) vs argon mean nearest-neighbor distance d for temperatures 32–34 K (triangles), 37–40 K (inverted triangles), 41–44 K (circles), 46–49 K (crosses), and 50–52 K (squares). Ar gas pressures were between 10^{-8} and 10^{-4} Torr. Typical error bars are shown for the (θ,d) measured from Fig. 2. The solid line is the prediction of Ref. 2.

Villain's calculations predict $\theta = 0°$ for rare-gas monolayers very close to registry ($d = 4.26$ Å),[5] where the linear response theory of NM is not valid. We were unable to obtain any (P, T) combination for Ar such that a well-ordered solid monolayer with $d > 3.95$ Å was formed. Thus our observations of $\theta \neq 0°$ for Ar do not contradict Villain's predictions. Moreover, $\theta = 0.0° \pm 0.5°$ has been observed for other incommensurate rare-gas monolayers: Kr, Fig. 2(d) of Ref. 3 and Fig. 3 of Ref. 9 ($d = 4.13$ Å); Xe, Fig. 1 of Ref. 4 ($d = 4.41$ Å). Our Ar observations indicate that the concentration of surface defects which might "lock in" an incommensurate overlayer to a high-symmetry orientation (such as $\theta = 0°$) is low on well-ordered portions of natural graphite crystals similar to those used in the Kr and Xe experiments. Thus the Villain and Novaco-McTague predictions, which are appropriate for different ranges of distance d, appear to be confirmed by different experiments.

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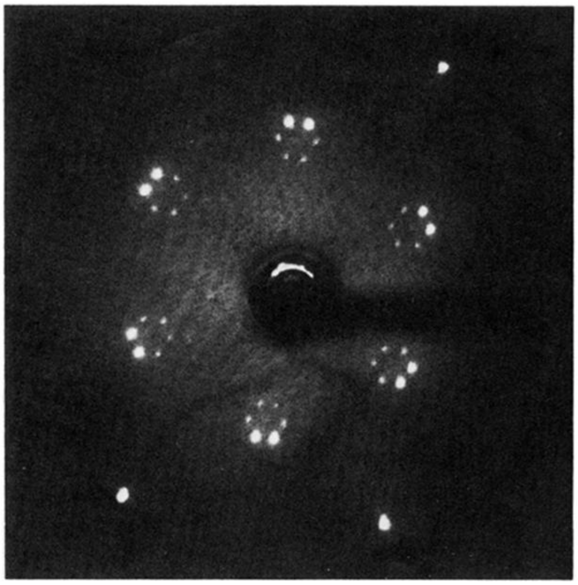

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