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Rotational epitaxy of a nontriangular structure: The δ phase of oxygen physisorbed on graphite

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Low-energy electron diffraction (LEED) observations of molecular oxygen physisorbed on graphite are reported. The structure of the low-coverage δ phase is shown to be a centered parallelogram and the rotational epitaxy is determined. At temperatures above 22 K where the LEED study was carried out, we find that the rotational epitaxy changes with coverage (the layer exhibits a Novaco-McTague effect). The possibilities of the structure melting anisotropically and of a low-temperature commensurate phase are discussed. Defect-stabilized or metastable structures are also observed.

Phase transitions in two-dimensional physisorbed layers offer the possibility of realizing interesting theoretical models. Adsorbed layers of diatomic molecules have different crystal structures than layers of spherical molecules and the phase transitions between these structures are of current interest.[1–3] The influence of the lateral potential variations of the substrate on the adsorbed overlayer can alter the character of the long-range order and the phase transitions of the adsorbed layer. These potential variations have also been observed to align incommensurate triangular solids along nonsymmetry directions of the substrate.[4–6]

Previous diffraction studies of molecular oxygen adsorbed on graphite have identified several phases[7–9] and have proposed structures for these phases. Neutron diffraction studies of the low-coverage δ phase proposed a triangular structure.[7] Subsequent x-ray diffraction measurements found a low Q-vector peak missed in the neutron study, and a centered-rectangular structure with the molecules lying parallel to the surface was proposed.[8] Additional data and further analysis[9] suggested that the unit mesh was actually a centered parallelogram with the skew angle γ between the two unit vectors of the centered-parallelogram mesh being slightly different from 90°. These studies were done on substrates which have a range of crystallite orientations, and thus information on the rotational epitaxy was not obtained. In this paper we present some low-energy electron diffraction (LEED) results for the low-coverage δ phase of O_2 adsorbed on single-crystal graphite. These results fill in the missing information and show how the rotational epitaxy of the O_2 layer changes with coverage (the Novaco-McTague effect).[4] This is the first time the Novaco-McTague effect has been observed for a nontriangular lattice and for diatomic molecules. In addition, the incommensurate centered-parallelogram unit mesh of the O_2 monolayer has no reflection symmetry axis, and so the layer can melt in an anisotropic way into a two-dimensional (2D) smecticlike or nematiclike liquid.[3]

The experimental apparatus and procedures were the same as those described in detail elsewhere,[2] with one exception. Because of the low equilibrium vapor pressure of O_2 layers at the temperatures studied, a doser was installed which allows a flux of gas to be directed at the sample, and so it was not necessary to backfill the system with gas. Since the vapor pressure was low, the experiments could be carried out at constant coverage for temperatures less than about 32 K. Below about 22 K the surface equilibrium time was longer than our typical experimental times (about 30 min), and so equilibrium data were obtained only for temperatures above 22 K.

The graphite crystals were cleaved in air with Scotch tape, baked to 1000 °C in flowing dry N_2 gas, and then placed in the ultrahigh-vacuum chamber. For some of the experiments, the chamber was baked to about 100 °C for about 24 h to facilitate the pump-down. Often an impurity LEED pattern was observed before this baking and the baking would always enhance that pattern. The impurity pattern was then routinely removed by electron bombardment.[2,10] For other experiments the chamber was not baked and in some cases the crystals showed no detectable impurity pattern.

The LEED diffraction patterns observed in this study can be explained as a superposition of patterns from six domains of the centered-parallelogram structure; one of these domains is shown in Fig. 1(a).

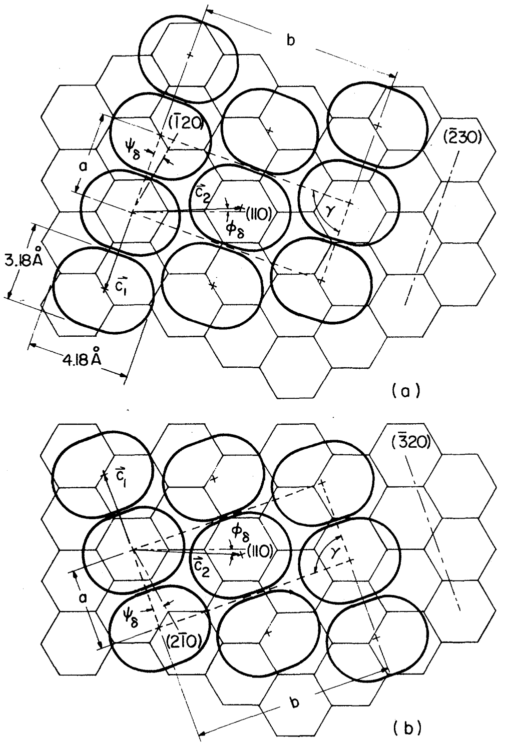

FIG. 1. Two of the six domains of the δ phase deduced from LEED diffraction patterns. The lattice constants a and b for a centered-parallelogram unit mesh, rotational epitaxy angles ϕ_δ and ψ_δ, and skew angle γ are shown, as well as the primitive lattice vectors $\vec{c}_1$ and $\vec{c}_2$. The domain shown in (b) is obtained by reflecting the overlayer structure in (a) about the graphite [110] direction.

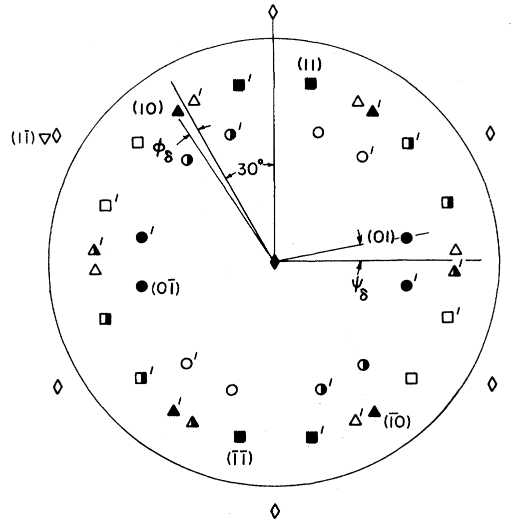

FIG. 2. Schematic drawing of a LEED diffraction pattern from the δ phase. The filled unprimed symbols are from the domain in Fig. 1(a) and the filled primed symbols are from the domain in Fig. 1(b). The indexing refers to the reciprocal net of the primitive mesh spanned by lattice vectors $\vec{c}_1$ and $\vec{c}_2$ in Fig. 1(a). The unprimed half-filled and open symbols are from domains rotated 120° and 240° from the domain in Fig. 1(a), respectively, and the primed half-filled and open symbols are from domains rotated 120° and 240° from the domain in Fig. 1(b), respectively. The graphite first-order spots are indicated by open diamonds and for an electron energy of 110 eV they are outside the field of view indicated by the large circle. The rotational epitaxy angles ϕ_δ and ψ_δ are also shown. The ($1\bar{1}$) reciprocal-lattice vector is indicated by the inverted triangle.

The primitive lattice vector $\vec{c}_1$ is almost aligned along the graphite [$\bar{2}30$] direction [a direction of a $(\sqrt{7}\times\sqrt{7})$ 19° unit mesh], and the primitive lattice vector $\vec{c}_2$ is almost aligned along the graphite [110] direction [one direction of the $(\sqrt{3}\times\sqrt{3})30°$ unit mesh]. The angles ϕ_δ between the graphite [110] direction and $\vec{c}_2$, and ψ_δ between the graphite [$\bar{1}20$] direction and $\vec{c}_1$, are used here to describe the rotational epitaxy of the δ phase. Note that although these two angles are not independent, they do provide somewhat different information about the rotational epitaxy. The exact orientation of the molecules in the plane has not been determined, but the parallel orientations shown were proposed in the x-ray studies[8,9] and are physically plausible.

Another domain of the δ phase is obtained by reflecting the overlayer structure shown in Fig. 1(a) about the graphite [110] direction; the resulting domain is shown in Fig. 1(b). The relationship between the domains in Figs. 1(a) and 1(b) is the same as that between two domains of the rotated triangular incommensurate structures of Ar or Ne on graphite.[5,6] However, even if ϕ_δ is zero, the domains are distinct since for O_2 the unit mesh is not triangular but a centered parallelogram. The diffraction patterns from Figs. 1(a) and 1(b) are shown by the filled symbols in Fig. 2. The labeled symbols represent diffraction spots from the domain shown in Fig. 1(a) and the indexing refers to the reciprocal net of the primitive lattice vectors $\vec{c}_1$ and $\vec{c}_2$. There are also four other domains which can be obtained by rotating each of the O_2 structures in Figs. 1(a) and 1(b) by 120° and by 240°; the complete resulting LEED diffraction pattern we observe is shown schematically in Fig. 2.

Although data were taken at constant coverage in the LEED experiment, the coverage could not be measured directly. However, for any coverage we can easily measure the melting temperature of the O_2 layer, and so in the region of the phase diagram[8,9,11] where this melting temperature is dependent on coverage (between the triple lines at 26 and

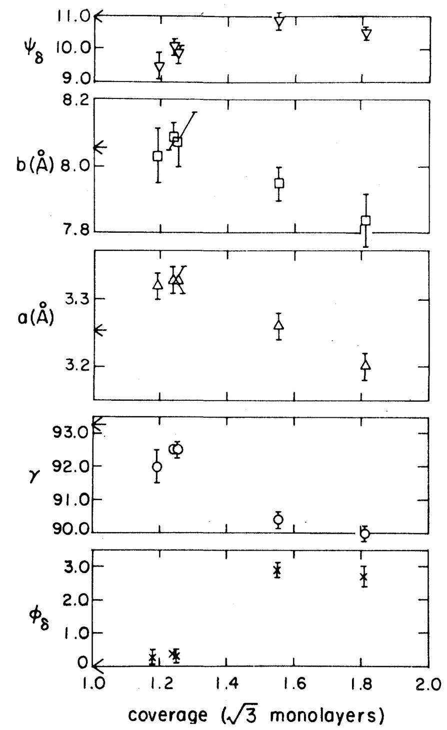

FIG. 3. Lattice constants a and b, skew angle γ, and rotational epitaxy angles ϕ_δ and ψ_δ at $T=24$ K as a function of coverage. The coverage is deduced from the melting temperature of the layer (see text), and since there may be some systematic error in the coverage, no error bars are shown. The lattice parameters for a $\begin{pmatrix}1&1\\-2&3\end{pmatrix}$ commensurate structure are shown by the arrows at the side.

32 K), we can then determine the coverage. Figure 3 shows the lattice constants a and b, the skew angle γ, and the rotational epitaxy angles ϕ_δ and ψ_δ at 24 K as a function of coverage. (A coverage of one corresponds to one complete $\sqrt{3}$ monolayer.) The linear coverage versus melting temperature curve of the x-ray[8,9] and heat-capacity[11] studies was used to convert the measured melting temperature into coverage.[12] As the coverage is increased and the lattice compresses, γ approaches 90° (the unit mesh approximates a centered rectangle) and the rotational epitaxy changes by several degrees. This change in ϕ_δ and ψ_δ with changing a and b is similar to rotations predicted by Novaco and McTague[4] for changing lattice constants of incommensurate triangular solids adsorbed on graphite. For O_2 the theory will be more complicated since the unit mesh is nontriangular and librational effects may be important. Also, since the O_2 unit mesh is very close to a $\begin{pmatrix}1&1\\-2&3\end{pmatrix}$ commensurate structure,[13] more terms may be needed in the expansion of the substrate potential[4] and the linear-response theory used by Novaco and McTague may not be adequate.[4]

The mesh of the δ phase does not have a reflection symmetry axis (at least for lower coverages where $\gamma \neq 90°$), and so the theory of dislocation-mediated melting for anisotropic layers of molecules considered by Ostlund and Halperin[3] suggests that the layer may melt into an anisotropic 2D smecticlike liquid. As the temperature is further increased above the melting temperature, the theory suggests that the layer may pass through nematiclike and quasi-isotropic phases. However, since the unit mesh of the δ phase is close to the $\begin{pmatrix}1&1\\-2&3\end{pmatrix}$ commensurate structure, the melting may not be adequately described by this theory. Also, as temperature increases the O_2 molecules may start to become perpendicular to the substrate and orientationally disordered and the theory does not include such effects. Heiney *et al.*[9] suggest the melting of the δ phase is first order, in contrast to the continuous transition described by the theory.[3] In spite of this, the nature of the fluid may still be similiar to that predicted by Ostlund and Halperin.[3]

At $T=15$ K and submonolayer coverages where the gas and solid coexist, the x-ray study finds $a=3.25$ Å, $b=7.985$ Å, and $\gamma=91.0°$.[8] These values are inconsistent with a $\begin{pmatrix}1&1\\-2&3\end{pmatrix}$ commensurate structure, which has $a=3.254$ Å, $b=8.064$ Å, $\gamma=93.1°$, $\phi_\delta=0.0°$, and $\psi_\delta=10.9°$. However, there is only a small difference between this value of a and that measured in the x-ray study at 15 K, and the value of ψ_δ that we measure above 22 K (see Fig. 3) is very close to 10.9°. (As mentioned earlier, no equilibrium LEED measurements were done below 22 K.) This suggests that the structure may become commensurate in the $[\bar{2}30]$ direction at low temperature. Indeed, magnetic-susceptibility measurements show a possible phase transition at $T=8$ K.[14] Additional work at low temperatures would be useful, but long equilibrium times at these coverages (hours to days[7,8,11,14]) make a LEED study difficult.

Sometimes another LEED pattern is also observed at the low coverages we have studied and it is shown schematically in Fig. 4. The O_2 solid phase that ordered (δ or δ') would sometimes depend on whether the impurity pattern discussed previously was initially present or not. We call the phase that produces this pattern δ' and have not studied it as extensively as the δ phase; its structure is shown in Fig. 5. The rotational epitaxy of this phase is very different from that of the δ phase, but at the temperatures and coverages that we have studied the δ' phase, the other lattice parameters of this phase seem to be the same as for the δ phase for the same temperatures and coverages. A phase with nonequilibrium rotational epitaxy also seems to be present for the higher coverage ζ phase of O_2.[15]

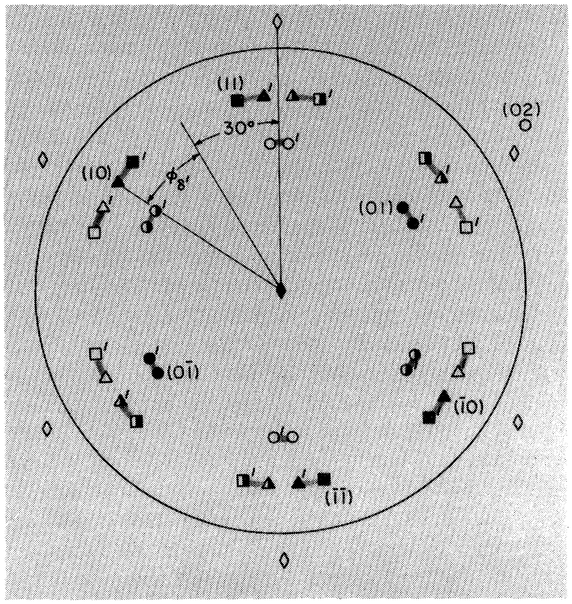

FIG. 4. Schematic drawing of a LEED pattern from the δ' phase. The gray areas between the spots indicate the azimuthal smearing that is always present. As with the δ phase there are six different domains of the O_2 crystal within the diameter of our electron beam. The labeled filled symbols are diffraction spots from the domain shown in Fig. 5 and the primed filled symbols are from a domain obtained by reflecting the overlayer structure in Fig. 5 about the graphite [110] direction. The other symbols are from domains obtained by rotations of these domains as in Fig. 2. The rotational epitaxy angle $\phi_{\delta'}$ and the first-order graphite spots are also shown. The (02) reciprocal-lattice vector is indicated by the open circle.

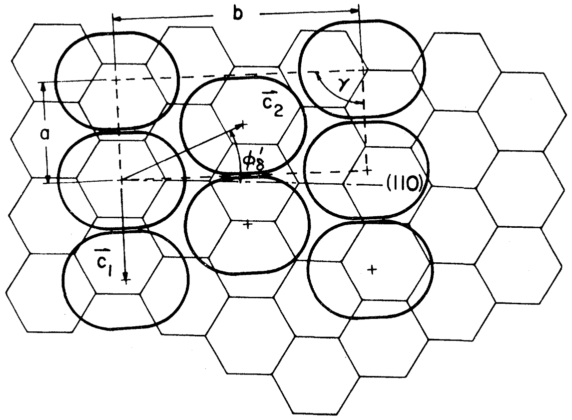

FIG. 5. Structure of one domain of the δ' phase deduced from LEED patterns similar to the one shown schematically in Fig. 4. An example of the lattice constants measured for a temperature of about 22 K and an unknown coverage greater than 1.6 is $a = 3.19 \pm 0.05$ Å, $b = 7.86 \pm 0.15$ Å, $\gamma = 90.0 \pm 0.3°$, and $\phi_{\delta'} = 25.7 \pm 0.6°$. Note that a, b, and γ are the same as for the densest δ phase (a coverage of 1.81 in Fig. 3), to within experimental error.

These phases may be stabilized by steps and/or impurity adsorption. LEED studies of Xe, Ar, and Kr and Ag(111) show that the alignment of the adsorbate triangular mesh is significantly different (about 25°–30°) from that predicted by theory[16] and this is attributed to the steps on the Ag(111) surface.

It is also possible that the energy of the centered-parallelogram structure on graphite has two minima at different rotational epitaxies as predicted for Xe on graphite.[4] The magnitudes of the (02) and (1$\bar{1}$) reciprocal-lattice vectors of the overlayer are very close (within 10%) to the magnitude of a first-order graphite reciprocal lattice vector. When the magnitudes of a substrate reciprocal-lattice vector and an overlayer reciprocal-lattice vector are approximately equal for triangular incommensurate overlayers, Novaco and McTague predict that the energy minimum can occur for a small rotation of the overlayer away from the substrate symmetry direction defined by the substrate reciprocal-lattice vector.[4] For nontriangular overlayers a similar result is expected, and when there are two overlayer reciprocal-lattice vectors whose magnitudes are close to a substrate reciprocal-lattice vector, there might be two such minima. As can be seen in Figs. 2 and 4, the δ phase seems to be in the energy minimum at a small rotation of the (1$\bar{1}$) reciprocal-lattice vector away from a graphite first-order reciprocal-lattice vector, and the δ' in the minimum at a rotation of the (02) reciprocal-lattice vector away from that direction. The δ phase may then be in the global minimum, whereas, the δ' is in a local minimum. Clearly, this argument is only qualitative and quantitative calculations would be necessary to make it more convincing.

The gray areas between the spots of Fig. 4 indicate the considerable azimuthal smearing that is always seen in the δ' phase and this smearing may be an indication of a defect-stabilized or metastable phase. Perhaps the structures on different regions of the substrate have different alignments and these alignments depend on the size of the region between the steps (or impurities). A distribution of these sizes would then cause the smearing. If the δ' phase is in a local minimum in the energy as a function of rotational alignment and that minimum is broad, then finite size effects may produce the smearing. Smearing is observed for Ne on graphite,[6] where the theory predicts a broad minimum.[4]

To summarize, the rotational epitaxy of the δ

phase of O_2 physisorbed on graphite is determined by LEED and the layer exhibits a Novaco-McTague effect. This is the first time this effect has been observed for a nontriangular structure. Although calculations have been made for O_2 molecules on a smooth graphite substrate,[17] we know of no quantitative predictions that have been made for the rotational epitaxy for nontriangular structures. There may be a phase transition at temperatures lower than those studied in these experiments and it may be a commensurate-incommensurate transition or perhaps a magnetic transition; additional diffraction studies would be useful. The structure of the δ phase is such that it may melt into a smecticlike or nematiclike liquid. Metastable or defect-stabilized phases are sometimes observed.

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