

Adsorption kinetics and thermal desorption measurements for oxygen layers on graphite

Hoydoo You* and Samuel C. Fain, Jr.

Department of Physics, University of Washington, Seattle, Washington 98195

(Received 18 September 1985; revised manuscript received 17 December 1985)

Adsorption kinetics and thermal desorption measurements of low-energy electron diffraction intensities are applied to extract information on coverages of structures occurring for oxygen layers physisorbed on the basal plane of graphite. The change in coverage required to compress the δ phase in other experiments on exfoliated graphite is most likely due to alternate-site adsorption, clustering, and/or intergranular condensation. The high-density ζ phase of oxygen previously studied by low-energy electron diffraction is found to be a monolayer structure. The exact structure of the bilayer ζ phase is not resolved.

I. INTRODUCTION

Many investigations of oxygen physisorbed on graphite have been made on large-area substrates such as Grafoil,¹⁻³ ZYX,^{4,5} and vermicular graphite.⁴ In such experiments the coverage is often expressed as the ratio of the amount of oxygen admitted to the substrate to the amount of Kr, H₂, D₂, or He which produces an optimal $\sqrt{3} \times \sqrt{3}$ phase on the same sample. However, the coverages required for a given phase of oxygen in various measurements on graphite of large surface area are found to be inconsistent with each other.¹⁻⁴ In previous reports of low-energy electron diffraction (LEED) measurements for O₂ on single crystals of graphite,⁶ the coverage scale determined in heat-capacity measurements on Grafoil² has been used. Adsorption kinetics and thermal desorption measurements are presented here to show that previous LEED measurements of the δ phase^{6,8} and ζ phase^{7,8} are at essentially monolayer coverages. Our observations also confirm that the coverage determination in experiments on large-area graphite is affected by alternate-site adsorption, clustering, and/or intergranular condensation.

II. EXPERIMENTS AND RESULTS

Graphite crystals at 25 K were exposed to a constant flux of O₂ molecules from an effusive source at 3 cm from the crystal surface. The diffraction pattern and the intensity of a graphite first-order reflection were monitored as a function of time. Measurements of the graphite intensity and the evolution of LEED patterns as a function of time are shown in Figs. 1 and 2. These two types of measurements were made with identical dose rates and initial conditions, and their consistency was carefully checked in a third measurement. Initially the oblique-unit-cell δ -phase pattern⁶ increases in intensity and the graphite beam linearly decreases in intensity, consistent with the growth of islands deduced previously.^{1,2} As the dose increases the δ phase is compressed into a centered-rectangular δ structure⁶ which we will call δ^* in the following discussions. The graphite intensity decreases more slowly, consistent with the attenuation no longer being proportional to coverage due to the compression of the layer. The apparent coexistence of the oblique low-coverage δ and the centered-rectangular higher-coverage δ^* phase may be partly due to slight nonuniformities in the dose rate across the 0.5 mm diameter of

the electron beam. The ratio of the dose at the end of the apparent δ - δ^* coexistence region (boundary between II and III) to that at the beginning (boundary between I and II) is 1.1 ± 0.1 . This is consistent with the ratio of monolayer densities obtained at 20 K from LEED measurements (1.07 ± 0.02),^{6,8} indicating that very little second-layer coverage is present in the δ^* phase. This demonstrates that the larger change in coverage required to compress the δ phase in Refs. 1, 2, and 4 is due to alternate-site adsorption, clustering, and/or intergranular condensation.

Shortly after the full monolayer of the δ^* phase is obtained, the ζ phase grows, coexisting with the δ^* phase until

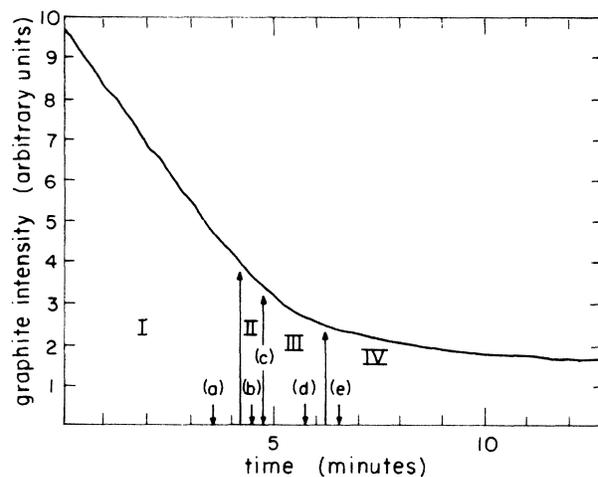


FIG. 1. The adsorption kinetic measurements of O₂ on graphite at $T = 25$ K. The diffracted intensity of one graphite first-order reflection was measured at 120 eV as a function of time by using a spot photometer. The sections for different structures are indicated and corresponding LEED patterns for the sections are given in Fig. 2. The almost perfect linear decrease of Sec. I is due to the island formation of δ phase. The subsequent slowdown in the decrease of intensity occurs because electron cross sections for molecules are overlapped and the proportionality of the decrease in intensity to the number of molecules no longer holds. Section II is the region of apparent δ - δ^* coexistence. Section III is the region of δ^* - ζ coexistence. Section IV is the region of the ζ phase. The ratio of time elapsed at the end of δ^* - ζ coexistence (boundary between III and IV) to that at the start of δ - ζ (boundary between II and III) is reproducibly about 1.4 for several runs. The times when the photos of Fig. 2 are taken in a separate run are approximately marked.

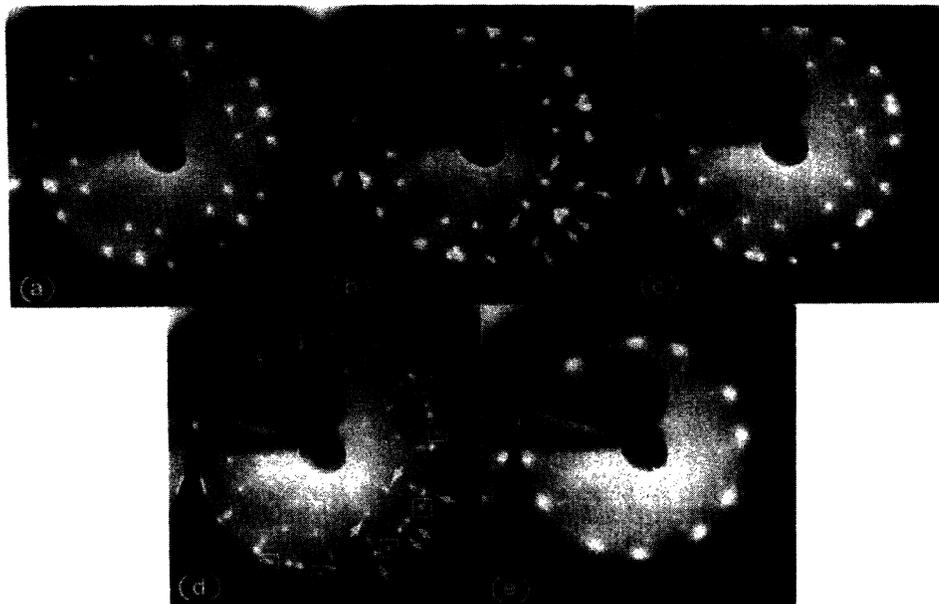


FIG. 2. The photos were taken at $T = 25$ K in a separate run under similar conditions at various energies of incident electrons to optimize each LEED pattern. (a) Submonolayer δ phase. (b) δ - δ^* coexistence region. (c) δ^* phase. (d) δ^* and monolayer ζ . (e) Monolayer ζ phase; photos (a)–(d) are taken at $E = 63$ eV and photo (e) is taken at $E = 83$ eV. The spots marked by squares in photo (d) are typical reflections from the ζ phase; multiple scattering spots from the ζ phase are also present in photo (d), but are not as evident at 83 eV energy of photo (e). Six typical spots from δ^* are marked with arrows in photos (b) and (d). The crystallites present in photo (a) are slightly different from those of photos (b)–(e) due to a slight adjustment in the electron beam direction.

only the ζ phase remains. The time elapsed at the end of the δ^* - ζ coexistence region is 1.40 ± 0.05 times that at the beginning of the coexistence region. This is slightly larger but remarkably close to the ratio of density of the ζ phase to that of the highest-coverage δ phase (≈ 1.33).^{2,5,8} Due to the low and constant temperature of the substrate, it is reasonable to assume that the sticking coefficient does not significantly change (the ratio observed can be well explained if the sticking coefficient is decreased by less than 20%). From the discussion in the previous paragraph, we see that the second-layer coverage in the δ^* phase is less than 10%. Thus, these measurements alone prove that the ζ phase also has very little second-layer coverage.

As soon as the monolayer ζ phase is completed (i.e., as soon as the coexisting δ^* phase disappears) the effusive source was closed and LEED patterns were studied for various temperatures. The LEED patterns at various temperatures are essentially identical to the LEED patterns of the previous LEED studies.^{7,8} When the temperature of the crystal with the monolayer is slowly increased one abrupt desorption step is observed at 47 K, confirming that the ζ phase is indeed a monolayer structure.

Adsorption of O_2 was repeated on the clean crystal with similar conditions except that the amount of the dose was twice as much as for completion of the monolayer ζ phase. The LEED pattern was similar to that of the monolayer ζ phase. When the temperature is increased in the same manner as for the monolayer, two distinctive desorption steps were observed at 32 and 47 K. The two desorption steps indicate that the ζ phase can be a bilayer structure. Within our experimental accuracy of 1% in lattice constant, the two layers are mutually commensurate as indicated by the resolution-limited spots.

The average q vector at 25 K for the bilayer ζ phase ($2.20 \pm 0.02 \text{ \AA}^{-1}$) seemed to be slightly smaller than for the monolayer ζ ($2.22 \pm 0.02 \text{ \AA}^{-1}$). However, this difference is very close to the resolution which is limited by the crystal quality and the LEED instrument. Broadening due to the unresolved spots for the bilayer ζ phase was also observed below 18 K. This broadening below 18 K suggests that the bilayer might undergo a structural transformation similar to that observed for the monolayer ζ phase⁷ in spite of the existence of the second layer. The bilayer ζ phase was not studied in the previous LEED measurements.^{7,8}

III. COMPARISON WITH X-RAY RESULTS ON THE ζ PHASE

From our experiments it is evident that the ζ phase at the end of the δ^* - ζ coexistence region is a monolayer structure. Therefore it is not an unreasonable assumption that the ζ phase at the end of δ^* - ζ coexistence region in previous experiments^{1–5} with large-surface-area graphite had negligible second-layer coverage and the real coverages were reduced by alternate-site adsorption, clustering, and/or intergranular condensation. Since the δ - ζ coexistence region ends at a filling of 2.6 times that for a $(\sqrt{3} \times \sqrt{3})R 30^\circ$ Kr phase in the low-resolution graphite x-ray study on ZYX graphite,⁴ the structure that occurs with a filling of 3.4 in the high-resolution ZYX x-ray study⁵ might be explained as a bilayer structure with a partially filled (not much more than 50%) top layer. When the top layer is only partially filled, at least two possible explanations of the two peaks at 2.20 and 2.24 \AA^{-1} of the high-resolution ZYX x-ray data⁵ can be proposed. (a) The bottom layer retains its monolayer lattice

constant, but the partially filled top layer is compressed as proposed by the authors of the high-resolution *ZYX* x-ray study.⁵ The authors suggested that the substrate field caused more tilt of the molecular axes away from the surface normal in the first layer than in the second, producing a more dense second layer. (b) The layer phase separates into regions of the monolayer and of the mutually commensurate bilayer structure. (This possibility was not discussed in the high-resolution *ZYX* x-ray study.⁵) The intensity due to the bilayer phase relative to that due to the monolayer phase will depend sensitively on the exact molecular axis arrangements in the bilayer phase,¹ as well as on the relative amounts of the two phases. The increase of the intensity of the 2.24 \AA^{-1} peak with coverage in the low-resolution data can be taken as an indication that this peak is due to the second layer in explanation (a) or from the bilayer in explanation (b). However, the intensity of the 2.20 \AA^{-1} peak should decrease with increasing coverage if explanation (b) were correct, which is not observed in the low-resolution *ZYX* x-ray data. Neither interpretation is easy to reconcile with the current LEED measurements of a smaller q vector for the bilayer ζ phase ($2.20 \pm 0.02 \text{ \AA}^{-1}$) than for the monolayer ζ phase ($2.22 \pm 0.02 \text{ \AA}^{-1}$). The LEED measurements are very sensitive to the top layer and the q vector for the bilayer ζ phase should be near 2.24 \AA^{-1} if the higher Q peak were due either to the top layer or to the bilayer phase.

Alternatively, it can be proposed that alternate-site adsorption, clustering, and/or intergranular condensation prevented the bilayer phase from growing and the 2.24 \AA^{-1} peak in the x-ray measurements above 18 K (Refs. 4 and 5) is entirely from bulk clusters. If this assumption is made, a consistent explanation of these LEED measurements at 25 K for the q vectors of the monolayer and bilayer ζ phase plus the high-resolution *ZYX* x-ray data at 27 K (Ref. 5) can be given. The reflection of LEED at 2.22 \AA^{-1} for the monolayer ζ phase corresponds to the peak of x-ray data at 2.20 \AA^{-1} and the ζ phase is a triangular structure at 27 K, as proposed previously.^{1,7} Then LEED data suggest that the bilayer ζ phase was never present in the x-ray measurements and is triangular for $T > 18 \text{ K}$, mutually commensurate, and more expanded than the monolayer ζ phase within experimental resolution of LEED. This model is, however, also not satisfactory because the 2.24 \AA^{-1} peak exists for a coverage of 2.7 for the low-resolution x-ray data on vermicular exfoliated graphite which is believed to have a much more open structure than *ZYX* and Grafoil and is hardly af-

ected by clustering.⁹ In addition, both low- and high-resolution x-ray data indicate that the 2.24 \AA^{-1} peak disappears near 37 K, which coincides with no bulk phase transition.

Several other models were considered in this study in a search for an explanation consistent with both the LEED and x-ray data for the ζ phase structures with coverages between the monolayer and the bilayer. However, none of the models could successfully explain all measurements currently available (Refs. 4, 5, 7, and the current LEED measurements). (Note the following: A layer structure and bulk were observed in a recent reflection high-energy electron-diffraction study, but the thickness of the layer structure could not be deduced and the observed lattice constants were different from both LEED and x-ray measurements.¹⁰)

In conclusion, our measurements presented here provide evidence that (a) the large change in coverage required to compress the δ phase in Refs. 1, 2, and 4 is due to alternate-site adsorption, clustering, and/or intergranular condensation, and (b) the ζ phase occurring for oxygen layers on graphite can exist as a monolayer. The structure of the monolayer ζ phase above 18 K appears to be triangular within our resolution as suggested in the previous LEED study.⁷ When two times the amount of oxygen necessary for the monolayer ζ phase is adsorbed, a bilayer structure that is mutually commensurate within our resolution is deduced. Further high-resolution studies either on large-area vermicular graphite or on a single crystal of graphite are required to determine the structures for bilayer ζ phases. It is desirable that the possibility of alternate-site adsorption, clustering, and/or intergranular condensation is carefully examined when a large-surface-area form of graphite is used for similar adsorption studies. Such examination will be possible if experiments similar to the adsorption and desorption experiments presented in this paper are performed on single crystal substrates.

ACKNOWLEDGMENTS

We would like to thank Jean Suzanne (Ref. 10) for providing us the idea of an adsorption kinetics study and Robert Birgeneau, Gregory Dash, Michael Toney, and Oscar Vilches for many useful discussions about oxygen on graphite. This work was supported by the National Science Foundation Low Temperature Program under Grant No. 80-06334.

*Current address: Physics Department, Brookhaven National Laboratory, Upton, N.Y. 11973.

¹J. P. McTague and M. Nielsen, *Phys. Rev. Lett.* **37**, 596 (1976); M. Nielsen and J. P. McTague, *Phys. Rev. B* **19**, 3096 (1979).

²J. Stoltenberg and O. E. Vilches, *Phys. Rev. B* **22**, 2920 (1980).

³R. Marx and B. Christoffer, *Phys. Rev. Lett.* **51**, 790 (1983).

⁴P. A. Heiney, P. W. Stephens, S. G. J. Mochrie, J. Akimitsu, R. J. Birgeneau, and P. M. Horn, *Surf. Sci.* **125**, 539 (1983).

⁵S. G. J. Mochrie, M. Sutton, J. Akimitsu, R. J. Birgeneau, P. M.

Horn, P. Dimon, and D. E. Moncton, *Surf. Sci.* **138**, 599 (1984).

⁶M. F. Toney, R. D. Diehl, and S. C. Fain, Jr., *Phys. Rev. B* **27**, 6413 (1983).

⁷M. F. Toney and S. C. Fain, Jr., *Phys. Rev. B* **30**, 1115 (1984).

⁸M. F. Toney and S. C. Fain, Jr. (unpublished).

⁹R. J. Birgeneau (private communication).

¹⁰J. A. Venables, J. L. Seguin, J. Suzanne, and M. Bienfait, *Surf. Sci.* **145**, 345 (1984); M. Bienfait, J. L. Seguin, J. Suzanne, E. Lerner, J. Krim, and J. G. Dash, *Phys. Rev. B* **51**, 983 (1984).

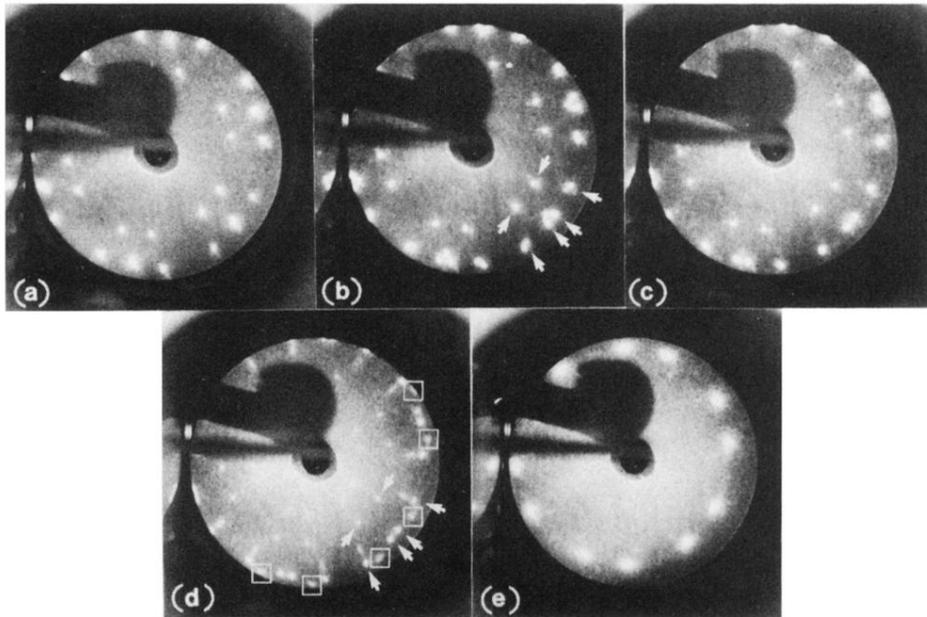


FIG. 2. The photos were taken at $T = 25$ K in a separate run under similar conditions at various energies of incident electrons to optimize each LEED pattern. (a) Submonolayer δ phase. (b) δ - δ^* coexistence region. (c) δ^* phase. (d) δ^* and monolayer ζ . (e) Monolayer ζ phase; photos (a)–(d) are taken at $E = 63$ eV and photo (e) is taken at $E = 83$ eV. The spots marked by squares in photo (d) are typical reflections from the ζ phase; multiple scattering spots from the ζ phase are also present in photo (d), but are not as evident at 83 eV energy of photo (e). Six typical spots from δ^* are marked with arrows in photos (b) and (d). The crystallites present in photo (a) are slightly different from those of photos (b)–(e) due to a slight adjustment in the electron beam direction.