RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 30, NUMBER 2 15 JULY 1984

Low-energy electron diffraction determination of the structure of the ζ phase of oxygen physisorbed on graphite

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(Received 13 April 1984)

Low-energy electron diffraction measurements on the ζ phase of diatomic oxygen physisorbed on the basal plane of graphite single crystals are reported for $12 < T < 28$ K. Two different monolayer phases are found with a phase transition between them near 18 K. The ζ 1 phase is stable below 18 K and has a slightly distorted triangular (oblique) unit mesh; the ζ 2 phase is stable above 18 K and has a simple triangular unit mesh. On imperfect crystals, another structure (ζ') is observed that is similar to ζ 2 except for a different rotational epitaxy; this structure is apparently stabilized by imperfections on the surface such as steps. These low-energy electron diffraction results are compared with those of other studies of the ζ phase.

Oxygen physisorbed on graphite has a number of interesting phases and phase transitions.[1-9] In this paper we report low-energy electron diffraction (LEED) measurements on the monolayer ζ phase in which the molecular axes are essentially perpendicular to the graphite basal-plane substrate.[10] At monolayer coverage, we find three possible incommensurate structures; the structure observed depends on the temperature and on the substrate quality. Two of these structures are apparently intrinsic to adsorption on perfect substrates: the ζ 1 phase, which exists for $12\text{ K} < T < 18$ K and has an oblique unit mesh; the ζ 2 phase, which exists for $18\text{ K} < T < 38$ K and has a triangular unit mesh. The third structure ζ' exists for $12\text{ K} < T < 38$ K and is similar to the ζ 2 phase except for a different azimuthal orientation with respect to the graphite symmetry axes; we believe the ζ' structure occurs because of steps on our imperfect graphite substrates. The structure of the ζ phase is important for understanding the nature of the ϵ-ζ 1 magnetic transition[1-6,11] and of the wetting behavior of oxygen on graphite.[4,12,13]

The experimental apparatus and procedures have been described elsewhere.[7] Below 30 K the equilibrium vapor pressure of the oxygen layers is very low, enabling the experiments described in this paper to be performed at constant coverage. After the crystal was cooled to about 25 K, oxygen was slowly added to the crystal through the doser[7] until the ζ 2 structure was observed without coexistence with the low-coverage δ-phase structure.[1-3] Separate measurements showed that for crystals in our geometry the coverage at this dose was just sufficient for one ζ layer.[14] The accuracy of temperature measurement is estimated to be 1 K near 18 K, with a greater uncertainty at lower temperatures.

Figure 1 shows the LEED pattern from the ζ 1 phase.[15] The ζ 1 phase produces 12 sets of three distinct spots within our LEED optics at 100 eV; one set is blocked by the doser and the electron beam tube for Fig. 1(b). These spots are as sharp [0.04 Å^{-1} full width at half maximum (FWHM)] as the best LEED patterns for the lower-coverage delta solid.[7,9] The spots in each triplet have equal intensities at all electron energies investigated. Figure 1 also shows diffuse arcs of intensity from the ζ' structure, which is on imperfect regions of the substrate. One of these arcs is located between the two white lines in Fig. 1(b); these arcs are always centered along the graphite directions, as shown in

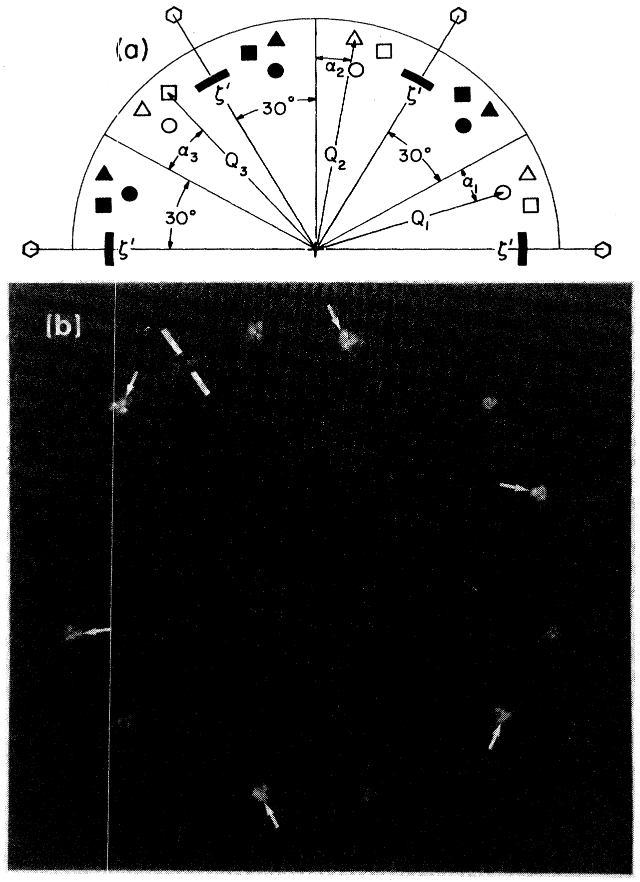

FIG. 1. LEED pattern from the ζ 1 and ζ' structures. (a) Schematic drawing with splitting of ζ 1 triplets exaggerated. The directions ϵ_l and magnitudes Q_l of three reciprocal lattice vectors from one domain are marked. The open symbols are from three domains rotated 120° apart; the filled symbols are from the other three domains produced by a reflection about the [110] graphite direction in Fig. 2. The hexagons indicate graphite spots outside the field of view at 100 eV indicated by the large circle. The scattering from the ζ' structure is also indicated (by filled arcs). (b) Photograph of LEED pattern near 12 K for 100-eV electron energy. 11 of the 12 sets of three closely spaced spots from the ζ 1 phase are observed. One of the six arcs of diffuse intensity from the ζ' structure is located between the two white lines. The arrows point to the six spots from the domain marked in (a).

Fig. 1(a). The ζ' structure will be discussed later in this article.

The incommensurate oblique unit mesh for the ζ 1 phase is shown in Fig. 2 for one of the six possible azimuthal orientations of the ζ 1 unit mesh on a given graphite crystallite. (For each of the three graphite symmetry directions, there are two possible domains related by a reflection about a graphite ⟨110⟩ direction, as also observed for the oblique unit mesh of the delta phase.[7]) All six domains were observed simultaneously in all measurements, although diffraction from three of the six was sometimes slightly more intense, as in Fig. 1(b). The 0.002 atomic unit charge contour which contains approximately 95% of the electron density of the molecules[8,16] is shown for an orientation exactly perpendicular to the graphite substrate. In Fig. 2 the space between the contours of adjacent molecules is larger than for the lower-coverage delta phase;[8] the extra room indicates that the molecules in the ζ 1 phase can be slightly tilted due to the substrate field. The unit mesh is only slightly distorted from a triangular mesh and is apparently incommensurate; however, the lattice vectors $\vec{a}_1$ and $\vec{a}_2$ are aligned close to graphite directions equivalent to the [$\bar{2}$30] and [120] directions shown in Fig. 2 ($\alpha_i = 10.9°$). One of the molecules is arbitrarily shown in the center of a graphite hexagon. The average values of the ζ 1 lattice parameters at $T < 16$ K are given in the figure caption.

Above about 18 K the LEED pattern consists of 12 spots which are slightly arced in the azimuthal direction (about 0.03 Å^{-1} radial and 0.06 Å^{-1} azimuthal FWHM). We believe this pattern is due to a distinct phase, ζ 2, which has a triangular unit mesh with two domains related by a reflection about a graphite ⟨110⟩ direction. The average values of the ζ 2 lattice parameters are given in the caption to Fig. 2.

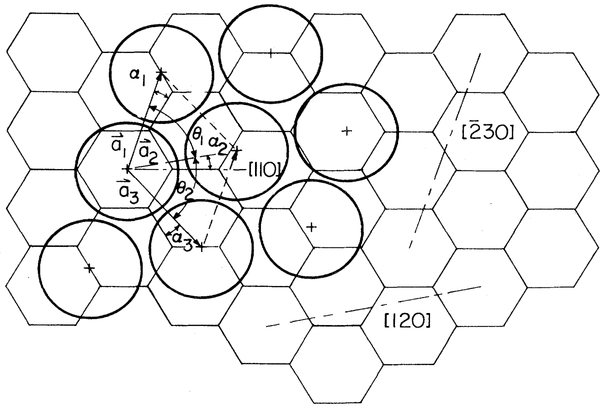

FIG. 2. Structure of one possible domain of the oblique ζ 1 phase on graphite. For the choice of unit cell shown by dashed lines, $\vec{a}_1$ and $\vec{a}_3$ are the basis vectors. The third vector $\vec{a}_2 = \vec{a}_1 + \vec{a}_3$ is given for convenience in comparing nearest-neighbor spacings in different directions. One of the orientational epitaxy angles (α_i) and three of the other lattice constants (nearest-neighbor spacings a_i and the interaxial angles θ_i) are sufficient to uniquely specify the structure. The average values of the ζ 1 lattice parameters below 16 K are $a_1 = 3.21 \pm 0.02$ Å, $a_2 = 3.34 \pm 0.03$ Å, $a_3 = 3.30 \pm 0.02$ Å, $\theta_1 = 60.4 \pm 0.2°$, $\theta_2 = 57.9 \pm 0.3°$, $\alpha_1 = 11.6 \pm 0.4°$, $\alpha_2 = 11.2 \pm 0.3°$, $\alpha_3 = 13.3 \pm 0.4°$. The ζ 2 structure is triangular with lattice parameters at 23 and 27.5 K of $a_1 = a_2 = a_3 = 3.30 \pm 0.03$ Å, $\theta_1 = \theta_2 = 60°$, $\alpha_1 = \alpha_2 = \alpha_3 = 12.1 \pm 0.5°$.

The slightly arced nature of the spots may be due to ζ 2 crystallites on different regions of the substrate having slightly different azimuthal orientations or to local realignments and strains due to imperfections on the substrate.[9] A somewhat larger spread in the azimuthal direction is observed for neon on graphite.[17] The average azimuthal orientation of about 12° from the graphite ⟨110⟩ directions is similar in the ζ 1 and ζ 2 phases, and a little smaller than the 17° value observed for neon on graphite, which has a similar nearest-neighbor spacing.[17] The small difference in azimuthal orientation between the ζ 2 phase of oxygen and neon is probably due to a different elastic response of the oxygen overlayer to the periodic substrate field.[18]

On the best crystal used (crystal I, one with resolution limited graphite diffraction and the lowest diffuse background scattering), the splitting into triplets shown in Fig. 1 changes only slightly below 16 K, but disappears above 18 K. For another crystal (crystal II) that was of somewhat poorer quality than crystal I (broader graphite spots and higher diffuse background), the triplets could be resolved near 12 K and appeared to broaden and merge as the temperature was increased above 12 K. By 14.2 K there appeared to be only 12 very broad spots, but the splitting into three spots was still apparent in the triangular spot shape. As the temperature was further increased, the spot size on crystal II decreased somewhat (the unresolved splitting decreased), until only 12 broad spots were observed at 18.6 K. The spot size on this crystal at 18.6 K (about 0.07 Å^{-1} radial and 0.10 Å^{-1} azimuthal FWHM) was larger than on crystal I at about the same temperature (0.03 and 0.06 Å^{-1}), which suggests that our inability to resolve the triplets is due to spot broadening caused by defects on crystal II.

Figure 3 shows the magnitude of the reciprocal-lattice vectors from the ζ 1 and ζ 2 phases on both crystals, along with their directions measured as shown in Fig. 1(a). The triplets in the ζ 1 phase were always well resolved for crystal I and the measurements were straightforward. When the splitting in the ζ 1 phase was not clearly resolved on crystal II, the observed LEED spots were assumed to result from three overlapping spots. These LEED data show that there is a phase transition at about 18 K from a monolayer phase with a slightly distorted triangular mesh (ζ 1) to a monolayer phase (ζ 2) with a simple triangular mesh. The accuracy of these measurements is not sufficient to determine whether the ζ 1-ζ 2 transition is continuous or first order.

Also shown on Fig. 3 are results of other diffraction measurements on the ζ phase, most of which are probably at higher coverages than our data. Only one diffraction peak was resolved in the neutron diffraction study on Grafoil;[1] the Q vector length of 2.21 Å^{-1} is shown as ×'s in Fig. 3. Low-resolution x-ray diffraction measurements on *ZYX* graphite substrates[3,6] detected three diffraction peaks at 15 K at the Q values of 2.14, 2.21, and 2.26 Å^{-1}, shown by the filled inverted triangles in Fig. 3. Although the Q values of these three peaks are close to those we observe in the ζ 1 phase, the intensities of the x-ray peaks at 2.21 and 2.26 Å^{-1} were significantly greater than that at 2.14 Å^{-1}. In addition, a high-resolution x-ray study on *ZYX* graphite[6] at a coverage similar to one studied in the low-resolution x-ray study found TWO peaks at 28 K at the Q values of 2.20 and 2.24 Å^{-1}, indicated by the arrows in Fig. 3(b). The x-ray investigators concluded that throughout its range of existence the ζ phase consists of two mutually incommensurate triangular layers[6] with a nearest-neighbor spacing at 28

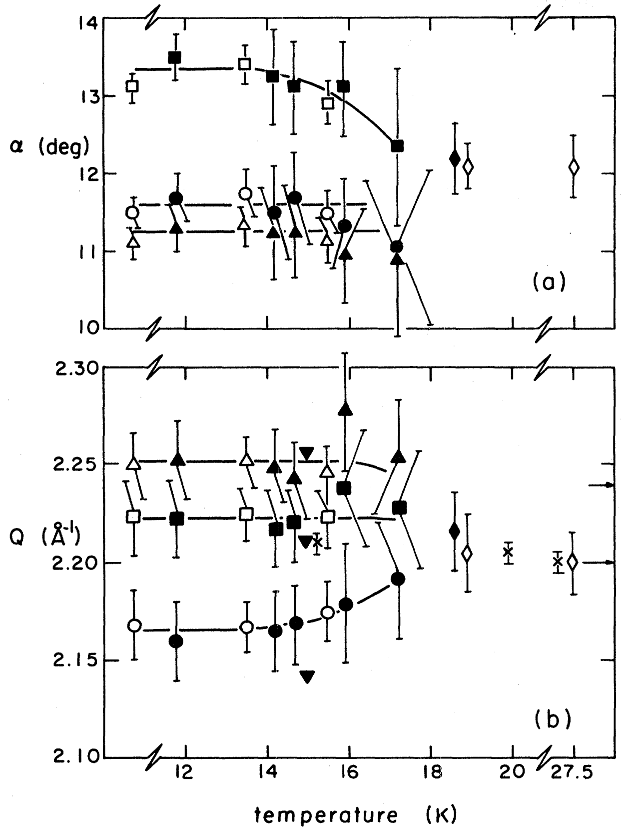

FIG. 3. Reciprocal lattice vectors as a function of temperature. The circles, triangles, and squares [see Fig. 1(a)] indicate LEED data from the ζ 1 phase; diamonds indicate LEED data from the ζ 2 phase. Filled symbols are from crystal II; open symbols are from crystal I. (a) Directions of the reciprocal lattice vectors measured as shown in Fig. 1(a). (b) Magnitudes of the reciprocal lattice vectors from this and other diffraction measurements (first-order graphite is 2.95 Å^{-1}).. Neutron diffraction data from Grafoil from Ref. 1 are indicated by ×'s. Filled inverted triangles indicate low-resolution x-ray diffraction data at 15 K from Refs. 3 and 6; the peak positions reported in Ref. 3 at 36 K are at essentially the same positions. Arrows at the right indicate high-resolution x-ray data (Ref. 6).

K of 3.24 Å in the top layer and 3.30 Å in the bottom layer. The peak at 2.14 Å^{-1} observed in the low-resolution study was then identified as a broad peak due to a Novaco-McTague modulation[18] between the two layers which would not be seen in the higher resolution study.[6]

This model of two mutually incommensurate triangular layers cannot describe our diffraction data from the ζ 1 phase. Due to the different environment of oxygen molecules in the top and bottom layers of two mutually incommensurate layers, multiple scattering in LEED might produce different intensities for the first and second layer diffraction spots as the energy is varied. In addition, if the LEED peak at 2.17 Å^{-1} were due to a Novaco-McTague–type modulation of the nearest-neighbor spacing[18] of two adsorbed layers plus multiple scattering between the layers, it would be considerably smaller in intensity and would probably have a different dependence of intensity on energy than that of the peaks at 2.22 and 2.25 Å^{-1}. In the ζ 1 phase the intensities of the spots in each triplet are identical at all energies to the accuracy with which we can observe them, ruling out the model of two mutually incommensurate layers.

In the ζ 2 phase our diffraction measurements alone cannot rule out the possibility of two mutually incommensurate layers with a difference in lattice constant of less than 1% and a difference in azimuthal angle of less than 1.4°. These are less than the 2% lattice constant and the 2° azimuthal angle differences deduced from the high-resolution x-ray study.[6] However, we believe that the difference between the LEED and x-ray studies is due to the difference in coverages investigated. The coverage in the high-resolution x-ray study was sufficient for two layers;[6] the coverage in our LEED study was just sufficient for one layer.[14] The single 2.20 ± 0.02 Å^{-1} LEED Q value at 27 K for the monolayer ζ 2 phase (Fig. 3) is the same as that of the peak identified as the first layer peak in the two-layer high-resolution x-ray study at 27 K.[6] This suggests that there is at most a 1% change (the uncertainty in the LEED measurements from the ζ 2 phase) in the first layer lattice constant when a second solid layer is condensed on the first layer at 27 K.

The condensation of bulk crystallites which occurred in the x-ray study at $T < 28$ K and coverages sufficient to give the ζ phase complicates the interpretation of the x-ray data. Reflection high-energy electron diffraction (RHEED) measurements found that bulk condensation on a single crystal occurred after the first few layers were deposited.[12,13] We observed no evidence for bulk condensation at the oxygen doses used for this study, which were considerably smaller[14] than those necessary to show bulk condensation in the RHEED experiment.

As mentioned earlier, six diffuse arcs of intensity are present in Fig. 1. We call the structure which produces this scattering the ζ' structure; it was present on all crystals at coverages similar to that of Fig. 1. This scattering was centered at $Q = 2.20 \pm 0.04$ Å^{-1} and was maximized at essentially the same energies as scattering from the ζ $1(T < 18$ K) or ζ $2(T > 18$ K) structures. However, the ζ' diffraction intensity relative to that of ζ 1 or ζ 2 and the ζ' radial and azimuthal spot widths depended in a complicated way on the graphite substrate, the oxygen overlayer preparation, and on the region of the substrate illuminated by the electron beam.[9] No distortion of the ζ' structure was detected at $T < 18$ K where the oblique ζ 1 structure was observed on the best crystals. Thus the ζ' structure is a simple triangular structure like the ζ 2 phase except for the different azimuthal orientation.

The alignment of the ζ' structure is along directions for which steps are likely to occur on imperfect graphite crystals. In physisorption of xenon, krypton, and argon overlayers on Ag(111) surfaces the azimuthal orientation of the overlayers was also along directions for which steps are likely to occur,[19] instead of the direction expected from the Novaco-McTague effect.[20] This similarity and other evidence discussed elsewhere[9] lead us to believe that the azimuthal orientation of the ζ' structure is caused by steps on our crystals, while the ζ 1 and ζ 2 phases are characteristic of perfect regions of our crystals. The absence of an observable distortion of the ζ' structure in LEED measurements below 18 K may result from the different effect of the substrate field for the azimuthal orientation caused by the steps or from some direct influence of the steps.

Large area substrates such as Grafoil and *ZYX* may also contain crystals for which the ζ' structure occurs. The peak in the 15-K low-resolution x-ray data at 2.21 Å^{-1} could include contributions from both the ζ 1 and ζ′ structures, making it more intense than the peak at 2.14 Å^{-1} from the ζ 1 structure; the peak in the 15-K x-ray data at 2.26 Å^{-1} certainly includes a contribution from bulk condensation.[3,6] The absence of a change at 15 K in the intensity of the 2.14- and 2.21-Å^{-1} x-ray peaks as the coverage was increased past the δ-ζ coexistence region[3] may indicate that only one layer of ζ 1 or ζ′ can form at 15 K.

The most likely cause for the distortion of the ζ 1 phase seems to be a combination of the lateral variation in the oxygen adsorption energy and of the tilting of the molecules toward the surface. The distortion may also be accompanied by a change in the short- or long-range magnetic order of the ζ phase. Recent magnetic-susceptibility measurements[21] show a small but definite jump near 17 K, which is about half the size of the jump in magnetic susceptibility at the ϵ-ζ transition.[4] This feature is reproducible and occurs at several coverages.[21] The closeness of the temperature of this transition to the ζ 1-ζ 2 transition indicates that there may be a connection between the distortion and the magnetic ordering.

In summary, we have observed two different high-coverage monolayer phases of oxygen on graphite and a phase transition between them at 18 K. The structure of the ζ 1 phase (12 K < T < 18 K) has a slightly distorted triangular (oblique) unit mesh; the ζ 2 phase (18 K < T < 38 K) has a simple triangular unit mesh. The differences between this study and previous x-ray investigations are most likely due to different surface coverages and to the absence of bulk condensation in the LEED experiments.

ACKNOWLEDGMENTS

We thank G. Felcher for supplying graphite crystals, R. J. Birgeneau and H. You for many useful discussions, J. Chui for remeasuring spot widths, J. G. Dash, E. K. Riedel, M. Schick, M. Sutton, J. Suzanne, and O. E. Vilches for helpful comments, and R. J. Birgeneau and S. Gregory for communicating and discussing their results prior to publication. This work was supported by the National Science Foundation Low Temperature Physics Program under Grant No. DMR 80-06334 and by a grant from the American Vacuum Society to M.F.T. for two years.

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[15] For Fig. 1 the thermometer indicated 10.2 K, a temperature where the ϵ phase should have been observed (Refs. 1, 2, 5, and 6). Another crystal with ζ phase present was cooled to as low as 5 K and observed for 90 min, but the ϵ phase was not observed. The most probable explanation for observing the ζ phase rather than the ϵ phase is that the equilibrium time was greater than typical experimental times of < 30 min for T < 12 K. This has also been observed for high coverages in Ref. 12. For the lower-coverage δ solid a similarly long equilibrium time was found for T < 22 K (Ref. 7); the difference of the surface equilibration times for the δ and ζ phases is possibly due to the different influence of defects on the two phases. A temperature difference between the crystal and the thermometer could cause the crystal to be warmer than the thermometer; this difference was found to be less than 1 K at 26 K, where the surface temperature could be checked by comparing the melting temperature of the δ phase with other measurements (Ref. 2).

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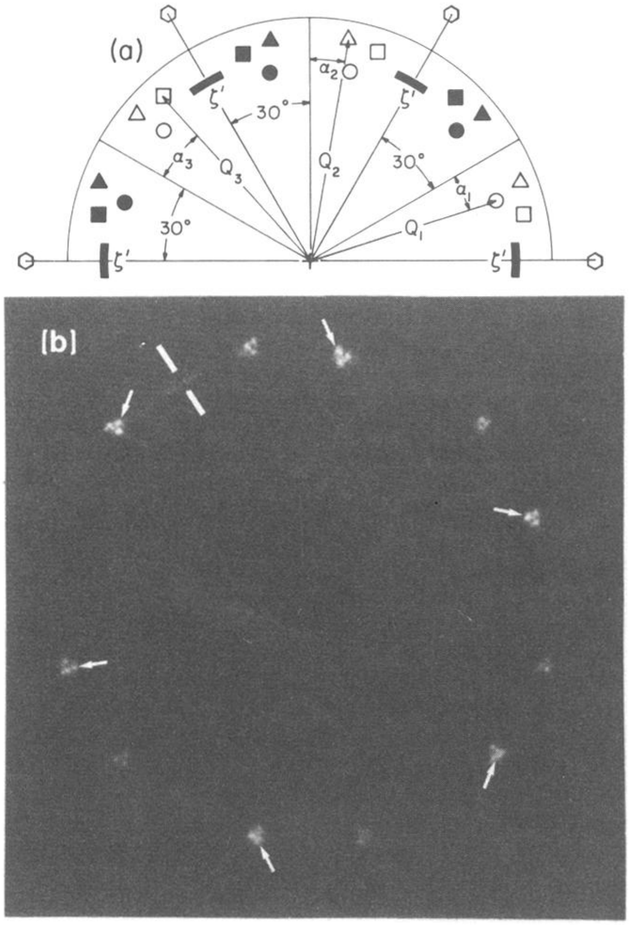

FIG. 1. LEED pattern from the ζ 1 and ζ' structures. (a) Schematic drawing with splitting of ζ 1 triplets exaggerated. The directions ϵ_i and magnitudes Q_i of three reciprocal lattice vectors from one domain are marked. The open symbols are from three domains rotated 120° apart; the filled symbols are from the other three domains produced by a reflection about the [110] graphite direction in Fig. 2. The hexagons indicate graphite spots outside the field of view at 100 eV indicated by the large circle. The scattering from the ζ' structure is also indicated (by filled arcs). (b) Photograph of LEED pattern near 12 K for 100-eV electron energy. 11 of the 12 sets of three closely spaced spots from the ζ 1 phase are observed. One of the six arcs of diffuse intensity from the ζ' structure is located between the two white lines. The arrows point to the six spots from the domain marked in (a).