Observation of Two-Dimensional Compositional Ordering of a Carbon Monoxide and Argon Monolayer Mixture Physisorbed on Graphite

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Commensurate monolayers of a mixture of 70% carbon monoxide and 30% argon on graphite are studied by neutron and low-energy-electron diffraction. A 2×2 superstructure due to 3:1 compositional ordering is observed below 25 K. The compositional ordering is most likely due to molecular-axis ordering of carbon monoxide molecules into a pinwheel pattern with argon atoms at the central sites of each pinwheel. Such a pinwheel structure has been predicted by Harris, Mouritsen, and Berlinsky for planar rotors with anisotropic interactions on a triangular lattice with vacancies.

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N_2 and CO solid monolayers physisorbed on graphite are known to order orientationally at low temperatures.[1-6] The ordered arrangements are predominantly determined by quadrupole-quadrupole interactions; a simple theoretical model of point quadrupoles on a triangular lattice[7] describes most of the observed structures.[2,4,6,8] Commensurate submonolayers of N_2 (Ref. 2) and CO,[4] triangular incommensurate monolayers of N_2,[6] and triangular incommensurate monolayers of CO (Ref. 4) are consistent with the theoretically predicted two-sublattice, in-plane (2-in) herringbone; two-sublattice, tilted-out-of-plane (2-out) herringbone; and pinwheel structures, respectively. Long-range end-to-end ordering of the C and O atoms in CO molecules seems not to occur either in the bulk α phase[9] or in the 2-in herringbone structure on graphite,[4] presumably because the structural effects of the dipole moment are much smaller than those of the quadrupole moment.[10]

Compositional ordering in two-dimensional (2D) adsorbed layers has been looked for numerous times[11-13] but has not been observed to date.[11,12] The present measurements were motivated by a theoretical study[14] of planar rotors with anisotropic interactions on a triangular lattice with vacancies and by previous experimental work on mixtures of N_2 and Ar.[12,13,15] (In an experiment, quadrupolar-coupled CO or N_2 molecules will play the role of planar rotors with anisotropic interactions, while Ar atoms, having no quadrupole moment, will act like vacancies.) Mean-field calculations predict that the compositionally and orientationally ordered pinwheel structure is the most stable configuration at low temperatures for compositions near 75% rotors and 25% vacancies.[14] Moreover, it is inferred from Monte Carlo calculations that the orientational ordering occurs as a continuous process with Ising exponents[14]—consistent with the universitality class of such transitions[16]—and that orientational and compositional ordering take place simultaneously. Heat-capacity measurements[15] indicated random dilution of the 2-in herringbone structure of N_2 near 25 K for Ar concentrations $< 10\%$; however, there was no evidence in neutron measurements[12] of long-range compositional ordering at 10 K in N_2-Ar mixtures. Low-energy electron diffraction (LEED)[13] showed only a short-range four-sublattice $(2\sqrt{3}\times2\sqrt{3})R30°$ ordering for a submonolayer $(N_2)_3Ar$ mixture suggestive of a local compositional ordering.

In this Letter, we present evidence of compositional ordering of a $(CO)_{0.7}Ar_{0.3}$ mixture on graphite, obtained from LEED and neutron-diffraction measurements on natural single crystals of graphite and a 25–30-m^2/g, loosely packed, exfoliated graphite powder, respectively. Below 25 K, a four-sublattice $(2\sqrt{3}\times2\sqrt{3})R30°$ commensurate structure for $(CO)_{0.7}Ar_{0.3}$ mixture was observed with LEED. Neutron diffraction showed that the four-sublattice structure is indeed compositionally ordered. Theory suggests that the ordered structure is the compositionally and orientationally ordered $(CO)_3Ar$ pinwheel arrangement shown in Fig. 1.

To obtain a given composition with an overall coverage of 0.98 ± 0.05 $(\sqrt{3}\times\sqrt{3})R30°$ monolayer for LEED studies the substrate was sequentially exposed at 38 K to CO and Ar at 5×10^{-9} Torr for times determined from pure CO adsorption measurements.[13]

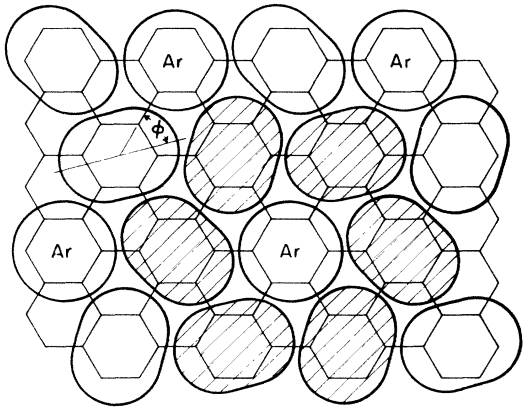

FIG. 1. The compositionally ordered pinwheel structure commensurate with the graphite surface. The theoretically predicted in-plane angle $\phi = 45°$ of the molecular axes is shown (Ref. 14). The contours of CO and Ar include 95% of the total charge densities. Carbon or oxygen ends of CO are not marked because of our assumption of end-to-end disorder. Six CO molecules surrounding an Ar atom are shadowed to emphasize the pinwheel pattern. An Ar atom and three orientationally ordered CO molecules form a unit cell.

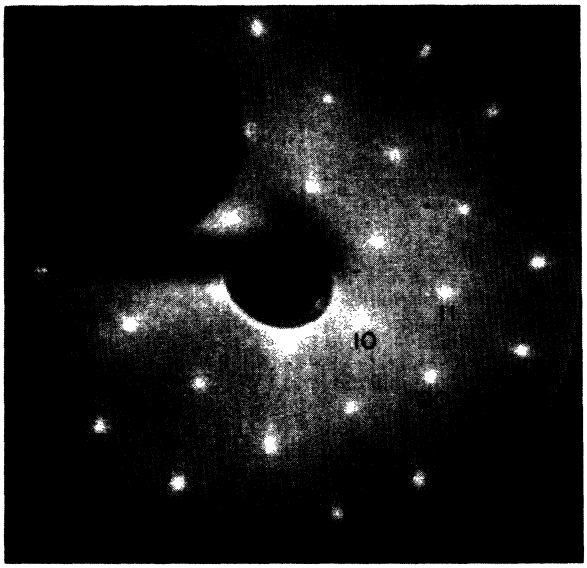

FIG. 2. LEED pattern at 20 K for $(CO)_{0.7}Ar_{0.3}$ obtained at normal incidence with 85 eV electrons. The shadows at the left are due to a dosing tube not used for the present measurements and to the electron drift tube. The 10, 11, 20, and 21 reflections are labeled in the photo.

Otherwise, the procedures were the same as previously described.[2] LEED measurements for 10 K $< T <$ 45 K showed only commensurate structures for $(CO)_{0.7}Ar_{0.3}$. Above 30 K the diffraction pattern was that expected for a submonolayer of orientationally disordered CO molecules randomly diluted with Ar. Between 30 and 25 K, the diffraction is that expected from a 2-in CO herringbone structure randomly diluted with Ar, i.e., similar to LEED patterns for the pure CO or N_2 2-in herringbone structure where certain reflections are missing at normal incidence because of a pair of glide-plane symmetries.[2,4,8]

Below 25 K, a $(2\sqrt{3}\times 2\sqrt{3})R30°$ LEED pattern with no missing reflections was observed as shown in Fig. 2. The 10 and 11 reflections would be missing for a 2-in herringbone structure[2,4,8] and the 10 reflections would be missing for a 2-out herringbone structure of the type observed for a triangular incommensurate N_2 monolayer.[6] Existence of all such reflections is consistent with a four-sublattice pinwheel structure on a triangular commensurate lattice. The simplest two interpretations of the observed pattern which are energetically possible for the quadrupole-quadrupole–coupled CO molecules are the commensurate CO pinwheel randomly diluted with Ar, predicted for small crystal fields,[7] and the compositionally ordered Ar-CO pinwheel, predicted in the limit of a large negative crystal field.[14]. In terms of Harris and Berlinsky's theory,[7] the decrease of the nearest-neighbor distance due to an increase of coverage changes the crystal field from a large negative value,[6] favoring an in-plane herringbone structure, to near zero, where a pinwheel structure is favored for pure CO. It appears unlikely that the pinwheel structure with random dilution would be favored when the lattice has the commensurate spacing of 4.26 Å. Thus the second configuration, shown in Fig. 1, seems more probable.

Analysis of LEED spot intensities to confirm directly the compositional ordering is complicated by multiple scattering of low-energy electrons. However, neutron-scattering experiments on a large–surface-area form of graphite can either confirm or rule out compositional ordering because of the validity of the single-scattering approximation and the large difference in scattering lengths of ^{40}Ar and CO.[17] Relative peak intensities are approximately estimated in Table I for a pure CO 2-in herringbone, a compositionally ordered pinwheel, and a randomly diluted CO pinwheel structure, with use of the theoretically predicted in-plane angle for point quadrupoles $\phi = 45°$.[7,14] Appropriate expressions for the peak intensities of powder-averaged line shapes were used,[18,19] with the assumption of end-to-end disorder of CO molecules, no preferred orientation of graphite, and no Debye-Waller effect. (A Debye-Waller factor would make the predicted 10 peak slightly larger relative to the 20 peak.) When we scaled calculated intensities to fit the 6000-count observed intensity of the 20 neutron peak at 1.702 $Å^{-1}$ for the pure CO herringbone structure, the calculated intensity of the 10 peak of compositionally ordered CO-Ar was found to be at least 500 counts for all ϕ values (see Fig. 1), indicating that the 10 neu-

TABLE I. Calculated and observed neutron peak intensities. (See text for details.) Estimates from Fig. 3 of the experimentally observed intensity at 10 K are given in parentheses.

Peak index (Figs. 2,3) / Q Vector (Å^{-1}) (Fig. 3)	{10} 0.851	{11} 1.474	{20} 1.702	{21} 2.252
Pure CO herringbone	0	0	6000 (6000 ± 200)	550 (350 ± 150)
$(CO)_3Ar$ compositionally ordered pinwheel	950 (800 ± 250)	400 (350 ± 200)	3400 (3200 ± 200)	500 (300 ± 150)
$(CO)_3Ar$ randomly mixed pinwheel	5	15	3750	300

tron peak is largely due to the difference in CO and Ar scattering lengths. For several two- or four-sublattice random mixtures the calculated intensities of the 10 peak never exceeded 100 counts.

All neutron scans were made with 2.5-Å wavelength neutrons on a triple-axis spectrometer set to detect only elastically scattered neutrons. As in the previous neutron-scattering experiments,[1,18] the background measured at 10 K without gas in the cell was subtracted from scans made with gas in the cell. The amounts of gas required to obtain an overall coverage of 0.95 ± 0.05 $(\sqrt{3}\times\sqrt{3})R30°$ monolayer with a given composition were determined from N_2 isotherms.[1,18] Diffraction scans for $(CO)_{0.7}Ar_{0.3}$ at 10 K were made only in the Q-vector range where the LEED pattern of Fig. 2 showed intense reflections. In addition, the $(CO)_{0.7}Ar_{0.3}$ mixture at 32 K and a $(\sqrt{3}\times\sqrt{3})R30°$ monolayer of pure CO at 10 K were also scanned at selected Q vectors to compare with $(CO)_{0.7}Ar_{0.3}$ at 10 K. All of the neutron profiles (with background subtracted) are shown in Fig. 3. Despite the negative difference counts (which result from a change in the small-Q profile when gas is introduced into the cell), it is evident that there is a 10 superlattice peak at $Q = 0.85$ Å^{-1} for $(CO)_{0.7}Ar_{0.3}$ at 10 K and that it has the expected, asymmetric Warren profile. LEED measurements show that pure commensurate CO at 10 K (Ref. 4) and $(CO)_{0.7}Ar_{0.3}$ at 32 K (Ref. 13) produce no detectable scattering near $Q = 0.85$ Å^{-1}. Using the equivalent neutron scans to define the background, we can place a lower limit on the 10 intensity of ~ 600 counts. An upper limit of ~ 1000 counts can be obtained from the raw difference counts. Thus we estimate the 10 superlattice peak intensity to be about 800 counts with an uncertainty of roughly 30%. Figure 4 shows the temperature dependence of the intensity of the 10 peak at 0.85 Å^{-1}. It first becomes detectable near 25 K as would be expected from the LEED measurements.

The observed intensities for $(CO)_{0.7}Ar_{0.3}$ at 10 K agree, within experimental uncertainties, with the calculated intensities for the compositionally ordered

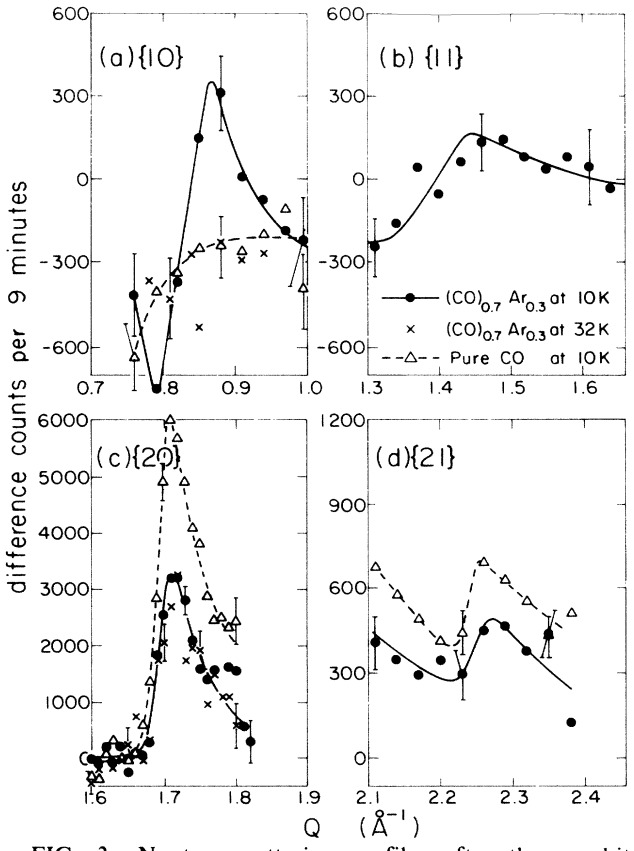

FIG. 3. Neutron-scattering profiles after the graphite background is subtracted. The 10 and 11 peaks for the mixture at 10 K (filled circles) are clearly distinguished from the background. The 21 peak at 2.25 Å^{-1} is sitting on the trailing edge of the very intense 20 peak. To estimate its intensity properly, the background from the 20 peak should be subtracted. The lines are guides to the eye.

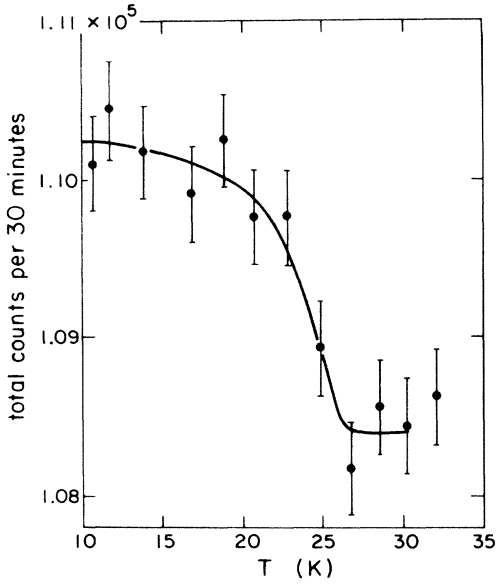

FIG. 4. Intensity of the 10 peak at 0.85 $Å^{-1}$ (see Fig. 3) for $(CO)_{0.7}Ar_{0.3}$ vs temperature. The solid line is a guide to the eye.

$(CO)_{0.7}Ar_{0.3}$[20] pinwheel structure (see Table I). *The relatively intense 10 neutron peak indicates—at the very least—that we are dealing with a compositionally ordered structure.* Since theory suggests[14] that pinwheel ordering induces compositional ordering of nonquadrupolar entities, it is likely that a pinwheel with $\phi = 45°$ is formed. It should be noted, however, that the measurements are not accurate enough to establish that the structure is orientationally (as well as compositionally) ordered and to obtain the angle ϕ.

We think it possible that long-range compositional ordering is observable in CO-Ar mixtures and not in N_2-Ar mixtures[12,13] (which were expected to be similar) because the larger quadrupole moment of CO (Ref. 4) moves the transition to a higher temperature. A higher compositional ordering temperature might permit equilibrium to be attained faster. LEED results for other CO-Ar compositions and for N_2-Ar mixtures and possible phase diagrams are discussed elsewhere.[13]

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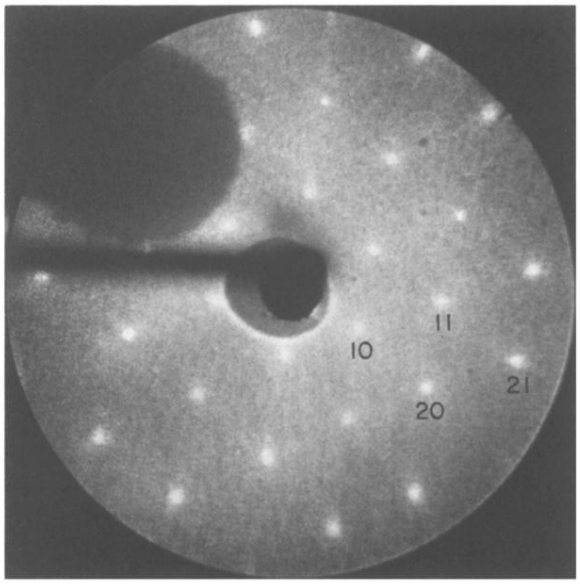

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