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High-order periodicity of physisorbed CO on graphite

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Abstract. A low-energy electron diffraction study of the high-density low-temperature phase of CO physisorbed on graphite has found evidence for high-order periodicity of the overlayer. The CO layer is locally incommensurate with the substrate, but new diffraction satellites found near the principal diffraction peaks indicate that the overlayer has high-order periodicity caused by interaction with the substrate corrugation.

1. Introduction

Simple molecules adsorbed on graphite have been found to display a wide variety of two-dimensional structures. The structures formed by molecules physisorbed on graphite can depend very sensitively on a number of competing interactions (e.g. surface coverage, molecular dipole moments, substrate corrugation, temperature). Because of this competition between many comparable small forces, the phase diagrams for molecules physisorbed on graphite are often quite rich in detail.

For a commensurate layer, the molecules of the overlayer sit in the minima of the molecule surface potential. On compressing the overlayer, the molecules are forced out of the commensurate sites, and in general the overlayer and substrate unit cells are no longer rationally related (i.e. the overlayer is incommensurate). However, the overlayer may still be affected by the substrate corrugation and the overlayer can buckle as it sits on the substrate corrugation. This buckling is called a mass-density wave (MDW) [1, 2], and the periodicity of this buckling is fixed by the misfit between the overlayer and the substrate corrugation. Mass-density waves will have a particular diffraction signature as satellites about the principal diffraction peaks. The MDW periodicity is a continuous function of the overlayer misfit (i.e. the coverage θ) on the substrate, and so these satellite peaks will be present over a range of coverage for the incommensurate overlayer.

A special case of a MDW can occur at certain coverages when the overlayer and substrate periodicities match [3, 4, 5]. The overlayer may still appear to be locally incommensurate, but is actually commensurate with a large unit cell. This high-order commensurate (HOC) structure will only occur at a certain coverage, and is stabilised by 'locking'—a few of the molecules in the unit cell are located in energetically favourable sites, so the entire overlayer is stabilised. As for the MDW, the HOC overlayer will be periodically distorted and display satellite diffraction peaks corresponding to this periodicity.

It is not possible to assert that an overlayer is HOC solely on the basis of the diffraction data [1, 2], as the resolution of available diffractometers is not sufficient to allow

measurement of the lattice parameters to the required accuracy. Recently it has been experimentally demonstrated [4, 5] that HOC overlayers can be distinguished from MDWs by their thermal expansion coefficients—a locked layer will be fixed to the substrate while an incommensurate MDW overlayer will expand freely as the bulk.

In this paper, we report measurements made by low-energy electron diffraction (LEED) for CO monolayers on graphite. For the high-coverage pinwheel phase, a diffraction pattern that shows satellite diffraction peaks characteristic of long-range ordering has been found, and we discuss the evidence for an incommensurate MDW and for a HOC structure.

2. Experimental details

The LEED system used to study physisorbed molecules on graphite is based on an electron energy-loss spectrometer (EELS) and is described in more detail elsewhere [6]. The high electron beam current of a conventional LEED system would quickly alter the structure of a physisorbed monolayer, so we have used the EEL spectrometer as a low-current LEED system. The incident electron beam is produced by the EELS monochromator, with an incident electron current of the order of 1×10^{-9} A. The LEED profiles are obtained by recording the elastically scattered electron intensity as the EELS analyser is rotated in the scattering plane about the sample, using a computer-controlled stepper motor.

The sample holder is similar to one previously described [7], and allows the sample to be cooled to ≈ 20 K using liquid helium. The graphite surface is prepared by cleaving the crystal in air with tape, and is cleaned in UHV by resistive heating. The sample is then cooled to the base temperature for the experiment within 15 min of being heated to an orange glow (≈ 800 K).

We use a highly oriented pyrolytic graphite (HOPG) crystal, which is a form of graphite having a surface composed of many microcrystallites (typically $\approx 1 \mu\text{m}$ in size) which are all oriented along the c axis to $\approx 1^\circ$ but azimuthally disordered. Our incident electron beam is much larger than a single microcrystallite, so the net effect of this disorder is to average the diffraction spots azimuthally into rings centred on the (00) beam. This property allows our diffractometer to sample all possible diffraction means by scanning in one plane, so we can measure the wavevector (k_{\parallel}) of the diffracted beam but we cannot determine the azimuthal direction of the beam.

The high-density CO monolayer phase was prepared by dosing the cold graphite surface with sufficient CO to allow multilayers of CO to form, and subsequently warming the sample to 35 K at which temperature the CO multilayers will desorb [8]. The chamber pressure rises due to the desorbing CO, and the high temperature is maintained until the pressure in the chamber has recovered. This preparation method produced reproducible high-density CO monolayer films, with a coverage of ≈ 1.18 ML as deduced from the observed lattice parameters.

3. Results and discussion

A LEED profile was obtained for the low-density $\sqrt{3} \times \sqrt{3}$ commensurate CO phase, and is shown in figure 1. The diffraction peak is seen at the $\sqrt{3}$ commensurate position ($k_{\parallel} = 1.71 \text{ \AA}^{-1}$), and is consistent with previous studies [8, 9]. Only a single peak is seen in the range of k_{\parallel} shown, as the other expected diffraction peaks are located at higher

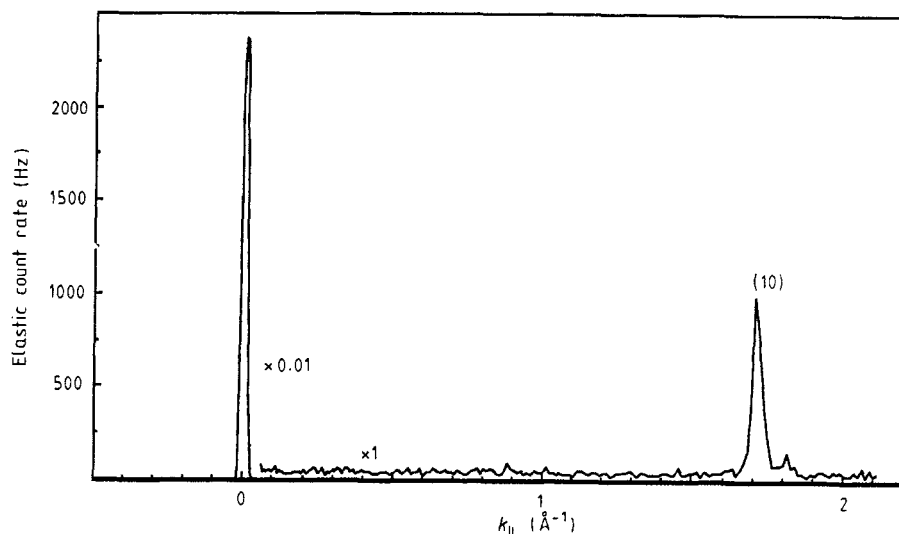


Figure 1. The LEED profile of the $\sqrt{3} \times \sqrt{3}$ commensurate CO monolayer. A single diffraction peak is found at the expected $\sqrt{3}$ position, within the resolution of our diffractometer. $E_i = 17.5$ eV, $T = 26$ K, $\theta_i = 63^\circ$.

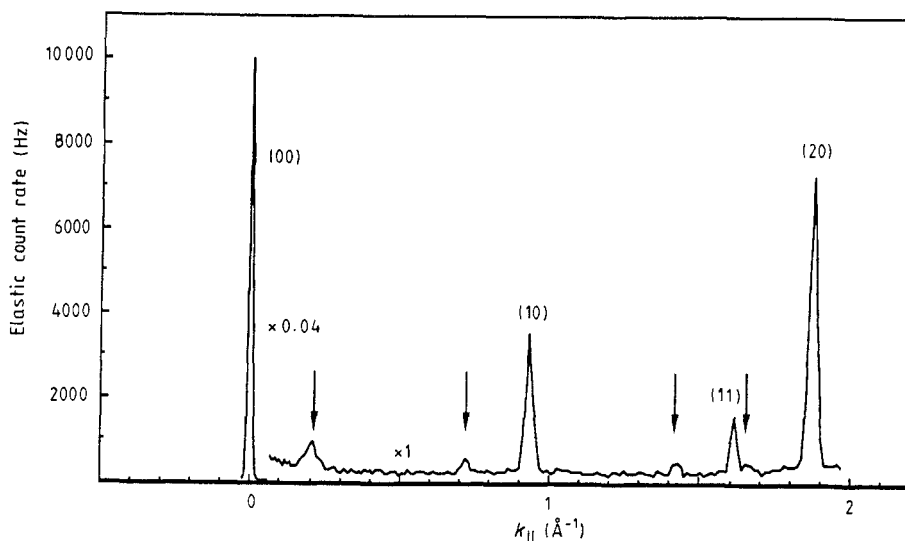


Figure 2. The LEED profile of the high-coverage pinwheel CO monolayer phase. The prominent peaks labelled (00), (10), (11) and (20) are expected for this pinwheel phase [9, 9], but the weaker satellite peaks marked by arrows indicate an additional long-range periodicity for this phase. $E_i = 17.5$ eV, $T = 26$ K, $\theta_i = 63^\circ$.

k_{\parallel} . The observation of this low-density commensurate phase diffraction peak at the expected position serves as a calibration of our diffractometer.

At higher coverage the CO overlayer is compressed, and the CO nearest-neighbour distance is no longer fixed to the $\sqrt{3}$ commensurate positions of the substrate. The observed LEED peaks are shown in figure 2, and are largely in agreement with those seen

previously. The compression of the adlayer moves the nearest-neighbour LEED peak (labelled (20)) to higher k_{\parallel} (1.88 \AA^{-1}), and the molecules in the layer become orientationally ordered into a pinwheel structure [8, 9], so the unit-cell size is doubled, which results in a new LEED peak (labelled (10)) appearing at $k_{\parallel} = 0.93 \text{ \AA}^{-1}$. The CO (11) diffraction peak is found at $k_{\parallel} = 1.62 \text{ \AA}^{-1}$. Several weaker diffraction features can also be seen in figure 2. The most prominent of these is at $k_{\parallel} = 0.21 \text{ \AA}^{-1}$, and other satellites are found at $k_{\parallel} = 0.72, 1.43$, and possibly at 1.66 \AA^{-1} . These satellite features are the focus of this paper†.

The wavevector differences between the principal diffraction peaks and their satellites are measured to be 0.21 \AA^{-1} for the (00), (10), and (20) peaks, and 0.19 \AA^{-1} for the (11) peak. These values of the separations are always measured for this high-density pinwheel phase, although sometimes the weaker satellites cannot be distinguished from the elastic background intensity. Several different model structures have been tried to fit the observed diffraction peaks, and we have found that only the MDW or HOC structures could be consistent with the observed satellites. Recalling that our diffractometer can only measure $|k_{\parallel}|$, we observe that the satellite of the (00) beam and those of the (10) and (20) beams have the same separation. This requires the satellite wavevector k_s to be in the same direction as $k_{(10)}$ and $k_{(20)}$. The satellite of the (11) peak will then only project part of its length ($|k_s| \cos 30^\circ \approx 0.182 \text{ \AA}^{-1}$), which is in reasonable agreement with the observed separation of that satellite. We thus conclude that the long-range periodicity observed occurs along the CO nearest-neighbour direction.

This long-range periodicity could be consistent with either the MDW or HOC models. An overlayer displaying a MDW will be rotated by a small angle ($\theta_r \approx 3^\circ$) with respect to the substrate, but due to the azimuthal averaging of our LEED pattern, we cannot measure this rotation. A HOC structure does not necessarily require a rotation, but could be rotated by a similar angle in order to lock to the substrate.

In order to distinguish unambiguously between a HOC and MDW structure, previous studies have monitored the diffraction patterns as a function of temperature [4, 5]—a locked structure will thermally expand with the substrate while an incommensurate layer will expand at a rate consistent with that of bulk solid CO. However, the resolution required (about 1 part in 1000, given the range of temperatures for the pinwheel phase and the solid CO thermal expansion coefficient) is beyond the capabilities of our diffractometer and we cannot resolve the question of the expansion (or lack thereof) of the CO overlayer.

To sum up, we have shown that there are LEED satellite diffraction peaks for the pinwheel phase of CO on graphite, which correspond to long-range periodicity of the overlayer. Further study of this system is necessary to determine the precise structure of this high-density CO phase. Studies of a single-crystal graphite surface using a higher-resolution technique (e.g. atom diffraction or x-ray diffraction) should be able to pin down the structure of this phase, and determine whether the layer is locked or floating (incommensurate) on graphite.

† Multiple scattering is not responsible for the observed extra diffraction peaks. The satellite peak positions are not consistent with any simple multiple-scattering channel. Also, upon warming the surface to form the high-density orientationally disordered incommensurate CO phase, the superlattice peaks disappear (as well as the (10) and (11) orientational ordering peaks).

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