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A LOW-ENERGY ELECTRON DIFFRACTION STUDY

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For Reference

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THE SURFACE STRUCTURES OF PHTHALOCYANINE MONOLAYERS AND VAPOR-GROWN FILMS: A LOW-ENERGY ELECTRON DIFFRACTION STUDY

J. C. Buchholz and G. A. Somorjai

Molecular Materials Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

Abstract

Monolayer structures and epitaxial growth of vapor-deposited crystalline phthalocyanine films on single-crystal copper substrates were studied using low-energy electron diffraction. At monolayer coverage, ordered layers of copper-, iron- and metal-free phthalocyanines were observed on both Cu(100) and Cu(111). With increasing film thickness, ordered multilayer structures of these phthalocyanines were also seen on both substrates at 300K surface temperature. All three phthalocyanines had identical monolayer and multilayer surface structures on Cu(100). On the Cu(111) substrate, the three phthalocyanines exhibited slightly different surface structures indicating the importance of the central metal atom in the interaction with the substrate that influences the monolayer surface structure and the ordering during crystal growth. The multi-layer crystalline films did not have surface structures characteristic of the bulk crystal structure but rather had a surface unit mesh compatible with a single molecule per unit mesh, oriented parallel to the surface. Electron beam damage and space charge effects were absent for film thicknesses up to 500-1000 Å.
Introduction

In recent years, low-energy electron diffraction (LEED) has been developed into a very important technique for determining surface atomic geometries of metals and inorganic semiconductors. Studies of the structural properties of the surfaces of organic crystals have been largely neglected. In this paper we report the application of low-energy electron diffraction to the study of the surface structure of several phthalocyanine crystals.

Many organic systems whose surface structures would be of particular interest are composed of molecules of high molecular weight and thus low vapor pressure making them suitable for study under vacuum conditions at room temperature. These systems include substances which exhibit unique surface structure and activity such as polymers, porphyrins and biochemical membranes. Although crystals of many of these organic solids can be grown from solution, the difficulties associated with removal of the solvents and transfer to the ultra-high vacuum conditions required for surface studies are severe. Instead, we have chosen to work with molecules that can be sublimed under vacuum conditions. Crystalline films were prepared by epitaxial growth upon condensation from the vapor onto single crystal surfaces.

The study of molecular solids presents several special difficulties when low energy electrons are used as experimental probes. These solids are electrical insulators although some (like Phthalocyanines) have sufficient conductivity at 300K to be classified as organic semiconductors. Thus there can be a build-up of surface space-charge under electron bombardment. Furthermore, electron bombardment can stimulate chemical
changes in the molecules. Despite these difficulties, low-energy electron diffraction has been successfully used to determine the surface structure of ice and naphthalene crystals epitaxially grown from the vapor on a Pt(111) substrate. The molecular crystals in these studies were grown at low temperature (-150K) because of the high vapor pressure of these materials. If the thickness of the crystal was maintained below 1000 Å, no difficulty with space-charge build-up was experienced. Electron beam damage to these materials, although present, was not so severe as to prohibit LEED measurements.

In this paper LEED measurements of the surface structure of Cu-, Fe- and metal-free phthalocyanines are reported. Epitaxially grown crystalline films of these materials were successfully grown on Cu(111) and Cu(100) substrate surfaces. All three phthalocyanines were found to yield ordered monolayers on both copper surfaces in the early stages of deposition. The initial layers formed on Cu(111) were similar but not identical for the different phthalocyanines indicating the influence of the central metal atom in the initial bonding to the metal substrate. Continued deposition produced a crystalline film consisting of oriented crystallites with surface planes inclined to the surface plane of the substrate. This growth plane was found to be identical for the different phthalocyanine molecules but different from that expected for bulk phthalocyanine crystals. The orientation of the crystallites with respect to the substrate, that is, the expitaxy, differed for the different molecules showing the effect on the growth habit of the central metal atom bonding to the substrate in the monolayer.
On the Cu(100) substrate, all three phthalocyanines studied exhibit the same surface structure for both a monolayer and a multilayer deposit. Although the phthalocyanine surface structure was similar to that found for a multilayer deposit on Cu(111), the surface plane was oriented parallel to the substrate surface.

Surface space-charge effects and electron beam damage were negligible during studies of these phthalocyanines.

**Experimental Procedures**

The phthalocyanine molecule is planar with a molecular structure as shown in Fig. 1. The molecules studied have H₂ (metal-free), copper or iron in the central position, M. Phthalocyanines deposited from the vapor generally grow as one of two polymorphic forms depending on deposition conditions.³ The structure of the stable β form of Cu-phthalocyanine is illustrated in Fig. 2. The crystal structure parameters of the phthalocyanines studied here are summarized in Table I.

The deposition and observation of the phthalocyanine films were carried out under ultra-high vacuum (UHV) conditions. The apparatus, shown schematically in Fig. 3, consists of a commercial, ion pumped LEED-Auger system with a base pressure of about 5x10⁻¹⁰ Torr. A quadrupole mass spectrometer and a sublimation source for production of a phthalocyanine beam were added to the basic system. The phthalocyanines were commercial powders⁵ used without further purification with the exception of an initial degassing in the UHV chamber for about one hour at ~500K. After this treatment, there is no increase in the system total pressure recorded by an ion gauge, located out of line-of-sight of the sublimator when the sublimator is operating. The mass spectrum for metal-free phthalocyanine,
obtained with the quadrupole mass spectrometer in line-of-sight of the sublimator, is shown in Fig. 4. Although the mass range of the quadrupole mass spectrometer does not allow the observation of the dominant parent ion peak in the mass spectrum, the fragments observed at lower masses are in general agreement with the previously reported mass spectrum for metal-free phthalocyanine. The constant ion gauge pressure indicates that the low mass peaks, not shown in the published spectra, are also fragmentation products where not accounted for by the system background spectrum.

At sublimation temperatures from 550-650K, deposition rates of from 1-10 layers/minute could be produced as judged by the rate of appearance and disappearance of the LEED pattern characteristic of monolayer coverage. The term monolayer refers to a single closely packed layer which, because of the large size of the phthalocyanine molecule, corresponds to about one molecule for every 30 copper atoms. The coverage is related to an incident flux by assuming a sticking probability of the phthalocyanine molecule on both clean copper and on previously deposited phthalocyanine of unity. This is justified since the effective beam pressure at the crystal (\(10^{-9}-10^{-8}\) Torr) is much higher than the room temperature vapor pressure of the phthalocyanines (\(10^{-14}\) Torr).

The substrates used were the (100) and (111) faces of copper. These surfaces were cut from single crystal rods and polished to within 1/2° of the specified orientation using standard metallographic techniques. Clean surfaces were produced in the UHV chamber by cycles of argon ion bombardment followed by annealing to 700K. A surface free of impurities, primarily sulfur and carbon, could be produced in this way, as demonstrated
by Auger spectroscopy. The LEED pattern after this cleaning treatment was also characteristic of a clean, well-ordered copper surface. 7

Results

The surface structure of the deposited phthalocyanine layer was obtained from the observed LEED pattern. The thickness of the phthalocyanine film was estimated by using the rate of deposition determined by the time required to obtain the diffraction pattern characteristic of a single layer of phthalocyanine molecules. The deposition rate can also be estimated by observing the rate of disappearance of the copper substrate diffraction beams. From estimates of the mean free path of a low-energy electron (15-200eV) before being inelastically scattered, 8 the rate of change of film thickness can be determined. Uncertainties in the determination of single layer coverage as in the electron mean free path result in an estimated uncertainty in the film thickness of about ±50% by both techniques. The only significant structural changes as a function of film thickness took place within the first few layers of the substrate surface, however, so that the multilayer film limit was reached rather quickly. The results stated for multilayer films are thus independent of film thickness for films up to 500-1000 Å thick, at which point the deposition was discontinued.

The phthalocyanine molecule was largely immune to damage by the incident electron beam both in the monolayer structure and in the multilayer film. The diffraction pattern was stable for periods of several hours under the LEED beam (15-200eV, ~1µA/mm²) and ~30 minutes in a beam for Auger spectroscopy (1000eV, ~5µA/mm²).

Surface space-charge did not interfere with the LEED experiment although diffraction patterns were not detectable from a multilayer
phthalocyanine film for incident beam energies greater than 25eV. Above this energy, there existed only a diffuse background, probably due to space charge effects. Sharp diffraction beams appeared when the energy was again lowered indicating no permanent damage to the phthalocyanine layer.

Deposition on a Cu(100) Substrate

The diffraction pattern observed for approximately monolayer coverage of Cu-phthalocyanine on Cu(100) is shown in Fig. 5. This LEED pattern is due to diffraction from domains, related to one another by the substrate symmetry elements, of a surface structure with a surface unit mesh as indicated in Fig. 6a. Knowledge of the unit mesh, determined from the LEED pattern, does not determine the position of the molecule on the surface however. Such a determination would require analysis of the diffraction beam intensities which is not yet feasible for molecules as large as phthalocyanine. From the size and shape of the unit mesh compared to that of the molecules, the orientation of the molecule on the surface can often be inferred. Figure 6b shows the size of the molecule relative to the surface unit mesh. It is apparent that the unit mesh is consistent with a structure in which the molecules lie parallel to the surface in a near close-packed configuration with one molecule per unit mesh.

For increased film thickness, the observed diffraction pattern is as shown in Fig. 7. This pattern is seen for film thicknesses from several layers to the maximum observed thickness (~1000 Å). The two-dimensional unit mesh responsible for this pattern is the same as shown in Fig. 6. Only the beam intensities have changed due to contributions to the diffracted intensity from layers beneath the surface which now consist of phthalocyanine molecules rather than copper atoms. The surface unit mesh
Thus still contains a single molecule oriented parallel to the exposed surface plane which is also parallel to the substrate surface. This exposed surface plane does not correspond to a plane in the bulk crystal structures of phthalocyanine shown in Fig. 2 and Table I. The deposited film has either a different bulk crystal structure than those previously reported or has a surface which is rearranged from its bulk structure. The same structures are seen for Fe- and metal-free phthalocyanine as well.

The initial adsorbed layer is known to play an important role in determining epitaxy in film growth. Several further experiments can be carried out to study the interaction of the initial layer with the substrate. If the phthalocyanine film is thermally desorbed from the substrate, the molecule remains intact, as observed with the mass spectrometer, with the exception of the first layer. Molecules adsorbed directly on the substrate are not removed but at higher temperature (~750K) decompose with a loss of nitrogen on the surface, as indicated by Auger spectroscopy. The molecules in the monolayer are thus strongly bonded to the substrate compared to the weaker intermolecular bonding in the phthalocyanine crystals.

The effect of the central metal atom on the phthalocyanine-copper substrate bonding was studied by repeating the above experiments for Fe- and metal-free phthalocyanines. For deposition on Cu(100), all the results were identical to those for Cu-phthalocyanine, including the thermal desorption results. This indicates that the dominant bonding to the Cu(100) substrate is through the phthalocyanine ligand rather than the central metal atom of the phthalocyanine.
Deposition on a Cu(111) Substrate

The LEED pattern observed at approximately monolayer coverage of Cu-phthalocyanine on Cu(111) is shown in Fig. 8. The surface structure responsible for this diffraction pattern consists of domains, related to one another by the substrate symmetry, characterized by the unit mesh shown in Fig. 9a. Again, superimposing the molecule on this unit mesh, as shown in Fig. 9b, suggests a structure with a single molecule per unit mesh oriented parallel to the surface. The location of the molecule is not known since complete surface structure analysis has not been performed for this structure. The position shown in Fig. 9b is only one possible configuration of the adsorbed molecule.

With increasing thickness of the phthalocyanine film a second surface structure develops. The diffraction pattern from this structure, shown in Fig. 10a, is seen superimposed on the previous, monolayer diffraction pattern. This indicates a very thin layer with this new structure since the mean free path of electrons with these energies, thus the penetration depth, is only on the order of 10 Å. It is likely that the second layer of phthalocyanine deposited on the surface already has this structure characterized by the unit mesh shown in Fig. 10b. This square mesh is similar to that seen for a multi-layer deposit of Cu-phthalocyanine on Cu(100) shown in Fig. 7. The structure of this second layer deposit is thus determined by packing within the phthalocyanine layer rather than by direct interaction with the substrate. The exposed surface plane remains parallel to the substrate at this point during deposition as indicated by the presence of a single specular reflection ((00) beam) in the diffraction pattern.
For increased film thickness (~500 Å), the LEED pattern is that shown in Fig. 11a. The unit mesh of the exposed surface plane is still square but the exposed surface is now inclined to the substrate surface resulting in extra specular reflections ((00) beams) as indicated in Fig. 11b. These specular reflections arise from crystallite surfaces inclined by an angle of about 12° to the substrate surface. The six specular reflections seen in Fig. 11a indicate crystallites related by the three-fold rotational symmetry of the Cu(lll) surface and a vertical mirror plane.

The variation of the surface structure with substitutions for the central metal atom in the phthalocyanine is shown by the diffraction patterns in Fig. 11. The behavior of all the phthalocyanines studied is qualitatively similar, that is, an ordered single-layer structure is initially formed followed by a multilayer structure with a surface plane inclined to the substrate. The monolayer structure unit mesh varies depending on the central metal atom as indicated in Table II. This variation, not observed for a Cu(100) substrate, indicates the contribution of the central metal atom to the bonding of the phthalocyanine monolayer to the Cu(lll) substrate.

The surface structures of the multilayer films are identical for the various phthalocyanines on the Cu(lll) substrate. Thus, the multilayer deposits exhibit the tendency of the phthalocyanines to develop nearly identical crystal structures regardless of the identify of the central metal atoms. However, the orientation of the crystallites, that is, the explitaxy, varies due to the structural differences in the monolayer. Fe-phthalocyanine, like Cu-phthalocyanine, reflects the three-fold rotational symmetry and mirror plane of the substrate in the crystallite orientation.
The exact angles between the substrate and crystallite axes, listed in Table II, are different than those for Cu-phthalocyanine however. For metal-free phthalocyanine the diffraction pattern, Fig. 11c, shows six-fold rotational symmetry in the position of the multilayer deposit specular reflections. The central metal atom thus plays a significant role in determining the orientation of the phthalocyanine molecule with respect to the substrate. This will be considered further in the next section.

Thermal desorption results again indicate that the first-layer phthalocyanine molecules are strongly bound since decomposition takes place before desorption. This is true for all three phthalocyanines studied indicating that the dominant bonding to the metal substrate is through the phthalocyanine ligand rather than the central metal atom.

Deposition on a Pt(111) Substrate

The deposition of Cu-phthalocyanine was also studied on a Pt(111) substrate. Only very diffuse fractional order beams could be observed for monolayer coverages of Cu-phthalocyanine. There is, thus, only very poor ordering in the surface layer. Because the diffraction beams were not well resolved, it was not possible to determine a surface unit mesh for this structure.

A multilayer deposit of Cu-phthalocyanine on Pt(111) was found to exhibit no ordered structure. This is in agreement with previous observations with other molecules that ordering in a multilayer depends very critically on the state of order in the initial monolayer film.²

Discussion

There are several important results obtained by these experiments:
1) Ordered monolayers of three different phthalocyanines, copper-, iron- and metal-free, are seen on two different faces of copper, the (111) and (100). The monolayer structures formed are different on the different crystal faces and on Cu(111) the different phthalocyanines all yield different monolayer structures.

2) Cu-phthalocyanine monolayers grown on a Pt(111) surface exhibit only very poor ordering. This poor monolayer order results in no observable ordering of the multilayer Cu-phthalocyanine film on this substrate.

3) Ordered multilayer deposits can be grown on both the Cu(111) and Cu(100) substrates. Electron beam damage to the phthalocyanine molecule is not observed. Space charge effects due to electron bombardment are not apparent below an incident electron energy of 25eV.

4) The surface structures observed for the multilayer deposits of the phthalocyanines on both substrate faces, Cu(111) and Cu(100), are not those of any plane in the bulk crystal structure of the phthalocyanines.

The monolayer surface structures observed for the various phthalocyanines on the two copper substrates are summarized in Table II. In all cases the size of the surface unit mesh is consistent with a surface structure consisting of the planar phthalocyanine molecule oriented parallel to the substrate with a single molecule per unit mesh. The bonding to the copper substrate is largely through the phthalocyanine ligand rather than through the central metal atom since the metal-free phthalocyanines are found, from the thermal desorption experiments, to be bound as strongly to the Cu(100) and Cu(111) surfaces as the Cu- and Fe-phthalocyanines. While the central metal atom in the phthalocyanines has no effect on the surface structures formed on Cu(100), it does play a
major role in determining the surface structure on Cu(111). Not only are
the monolayer structures different for the three phthalocyanines but the
epitaxy of the multilayer deposit indicates a fundamental difference in
the interaction of the metal and metal-free phthalocyanines with the Cu(lll)
surface. The metal-free phthalocyanine film grows, in the multilayer
deposits, as a number of individual domains or crystallites each yielding
its own diffraction beams including its own specular reflection, since
the surface planes are not parallel to each other. The metal-free phthalo-
cyanine film exhibits six-fold symmetry in crystallite orientation (six-
fold symmetry in crystallite specular reflections seen in Fig. 11c, d).
The Cu(111) surface, although six-fold symmetric in the atomic positions
in the top layer, is only three-fold symmetric when the atomic positions
of the second and third layer layers are included (abc stacking of an fcc
crystal). Thus the metal-free phthalocyanine interacts with the substrate
surface either through non-localized interactions such as Van der Waals
forces or bonds with only electrons in the copper which exhibit six-fold
symmetry, that is the metallic s-electrons of the top copper layer.
Copper- and iron-phthalocyanines, however, exhibit three-fold symmetry in
crystallite growth Figs. 11a,b,e,f). Thus the addition of a metal atom
in the phthalocyanine reduces the apparent symmetry of the substrate.
The central metal atom is thus involved in bonding to the second layer
copper atoms or to three-fold symmetric electron orbitals, for example,
d orbitals, of the surface copper atoms.

Deposition of Cu-phthalocyanine on a Pt(111) surface resulted in
only poorly ordered monolayer structures and no ordering of multilayer
structures. This demonstrates the importance of the details of the
adsorbate-substrate interaction even for very large adsorbates which overlap tens of surface atoms. The absence of an ordered multilayer structure on this substrate indicates the role of an initially ordered monolayer in controlling epitaxial growth. The difference in behavior of the copper and platinum substrates is possibly due to several causes. The electronic structure of the two metals is very different. Platinum bonds aromatic molecules very strongly through interaction with the partially filled d bands. Copper, with a filled d band does not strongly adsorb aromatic hydrocarbons. Thus the adsorbed phthalocyanine molecules will be less strongly influenced by the substrate and may themselves determine the packing on the surface. The lattice constant is considerably different (~0%) for copper and platinum which may also affect ordering of the phthalocyanine monolayer. Work is planned on a silver substrate which has a lattice constant nearer to that of platinum but electronic properties more like copper in an attempt to determine which of these factors is more important.

Ordered multilayer deposits of phthalocyanine molecules could be observed by low-energy electron diffraction with no apparent electron beam induced chemical effects. This appears consistent with the general trend for molecules with highly conjugated electron systems to be more stable under electron bombardment than other organic molecules. Surface space charge accumulation did not interfere with low-energy electron diffraction measurements although the diffraction pattern disappeared abruptly at ~25eV, being replaced by only diffuse halos above this energy. Since the pattern reappeared equally abruptly when the energy was lowered, there was clearly no permanent surface damage. This behavior is thus attributed
to a build-up of surface space-charge possibly due to an unfavorable secondary electron emission coefficient.

The surface structures observed for the multi-layer phthalocyanine films are summarized in Table II. These structures do not correspond to planes of either of the previously reported crystal structures of vapor deposited phthalocyanine films\textsuperscript{9} since the unit mesh constants reported in this work are considerably smaller than those previously reported. Our unit mesh dimensions correspond much closer to a unit cell containing one molecule rather than for example the four molecules per cell reported for α-phthalocyanine. This structural difference could be due to either a rearrangement of the surface region or the growth of an entirely different crystal structure due to the constraints of the substrate. The latter situation is very possible since the deposition conditions reported previously\textsuperscript{8} were very different than those used in this experiment. Our substrate was a clean metal surface maintained at room temperature whereas reported results were for deposition on muscovite and alkali halides maintained at 423K. No epitaxy was reported below this temperature. Our observation of epitaxial growth at room temperature is possibly the result of using a metal substrate and clean surfaces even at room temperature which was not the likely case in the previous work that was carried out in poorer vacuum.
There are several important conclusions that can be made as a result of this study. 1) The surface structures of high molecular weight organic crystals can readily be studied by LEED. Ordered surfaces have been obtained by growth under appropriate experimental conditions of temperature and epitaxy. Thus, it appears that surface structures of other complex organic systems such as polymers and biopolymers may also be investigated using this technique. 2) The chemical bonding of the organic monolayer is sensitive to the crystal face of the substrate. In turn, the bonding between the first organic layer and the substrate greatly influences the growth habit and the surface structure of the growing organic crystal. As a result, 3) the surface structure of the organic system may not correspond to a plane in the bulk crystal structure of the material. These observations will certainly facilitate the investigation of the surface structures of other, perhaps more complex, organic crystals in the future.

Acknowledgement

This work was supported by the U. S. Energy Research and Development Administration.
<table>
<thead>
<tr>
<th>Table I</th>
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<tbody>
<tr>
<td>Summary of bulk crystal structure data for metastable α form and stable β form of phthalocyanines</td>
</tr>
</tbody>
</table>

**Metastable α Form**

<table>
<thead>
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<th>Fe-Phthalocyanine</th>
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<td>a</td>
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<tr>
<td>b</td>
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<tr>
<td>c</td>
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<tr>
<td>β</td>
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<td>Space Group</td>
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**Stable β Form**

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<td>a</td>
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<tr>
<td>c</td>
<td>14.8 Å</td>
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<td>β</td>
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<tr>
<td>Space Group</td>
<td>P2₁/a</td>
<td>P2₁/a</td>
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</tr>
</tbody>
</table>
Table II

Summary of surface unit mesh data determined in this work for both single layer and multilayer structures of several phthalocyanines. \( \vec{a} \) and \( \vec{b} \) are the surface unit mesh vectors which are at an angle \( \gamma \) to each other. \( \vec{a} \) is at an angle \( \delta \) to the indicated direction in the substrate surface. The exposed surface plane is inclined at an angle \( \theta \) to the substrate surface where indicated.

### Single Layer Structures

#### Cu(100) Substrate

<table>
<thead>
<tr>
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<th>Phthalocyanine</th>
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<td>13.7 Å</td>
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<td>( \vec{b} )</td>
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<tr>
<td>( \gamma )</td>
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<td>90°</td>
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</tr>
<tr>
<td>( \delta )</td>
<td>22.5°</td>
<td>22.5°</td>
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</table>

\( \delta \) measured to (110) direction

#### Cu(111) Substrate

<table>
<thead>
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<th>Cu-Phthalocyanine</th>
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<td>( \vec{a} )</td>
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<td>( \vec{b} )</td>
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<td>( \gamma )</td>
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<td>( \delta )</td>
<td>10.25°</td>
<td>8°</td>
<td>11°</td>
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\( \delta \) measured to (110) direction

### Multilayer Surface Structures

#### Cu(100) Substrate

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#### Cu(111) Substrate

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<th>Fe-Phthalocyanine</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \vec{a} )</td>
<td>11.0±.5 Å</td>
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<tr>
<td>( \vec{b} )</td>
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<td>11.2±.5 Å</td>
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<tr>
<td>( \gamma )</td>
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<td>15°</td>
</tr>
<tr>
<td>( \theta )</td>
<td>12°</td>
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</tbody>
</table>

\( \delta \) measured to (110) direction

\( \theta \) measured between surface plane and surface normal
**Figure Captions**

**Fig. 1** The phthalocyanine molecule.

**Fig. 2** Orientation of molecules in the bulk crystal structure of the stable \( \beta \) form of metal-free phthalocyanine. After Kitaigorodskii. \(^4\)

**Fig. 3.** Experimental system. 1) Single crystal substrate, 2) Four grid LEED optics, 3) Oven and collimators for sublimation of phthalocyanines, 4) Quadrupole mass spectrometer, 5) Ion gun for argon ion bombardment, 6) Ion pumped vacuum system.

**Fig. 4** Mass spectrum obtained for metal-free phthalocyanine for a sublimator temperature of 660K.

**Fig. 5** LEED pattern at normal incidence for monolayer coverage of Cu-phthalocyanine on Cu(100). Incident beam energy 21eV.

**Fig. 6** a) Surface unit mesh (II) responsible for the diffraction pattern in Fig. 5. \( |\vec{a'}| = |\vec{b'}| = 13.7 \text{ Å} \). Unit mesh (I) is that for clean Cu(100). \( |\vec{a}| = |\vec{b}| = 2.55 \text{ Å} \).

b) Cu-phthalocyanine molecule superimposed on the surface unit mesh. \( |\vec{a'}| = |\vec{b'}| = 13.7 \text{ Å} \). Cu-phthalocyanine is shown with a Van der Waals radius of 1.2 Å attributed to the hydrogen atoms.

**Fig. 7** LEED pattern at normal incidence from a multilayer film of Cu-phthalocyanine on Cu(100). Incident electron energy 15eV.

**Fig. 8** LEED pattern near normal incidence from a monolayer deposit of Cu-phthalocyanine on Cu(111). Incident electron energy 14eV.

**Fig. 9** a) Unit mesh (II) responsible for the diffraction pattern in Fig. 8. \( |\vec{a'}| = |\vec{b'}| = 12.6 \text{ Å} \). Unit mesh (I) is that for a clean Cu(111) surface. \( |\vec{a}| = |\vec{b}| = 2.55 \text{ Å} \).

b) Cu-Phthalocyanine superimposed on the surface unit mesh.
\[ |\mathbf{g}'| = |\mathbf{g}''| = 12.6 \text{ Å}. \]

**Fig. 10**

a) LEED pattern near normal incidence for a two-layer deposit of Cu-phthalocyanine on Cu(111). Incident electron energy 14eV.
b) Unit mesh of second layer Cu-phthalocyanine deposit. \[ |\mathbf{g}''| = 11.2 \text{ Å}. \]

d) LEED pattern near normal incidence for a multilayer deposit of Cu-phthalocyanine on Cu(111). Incident electron energy 14eV.
b) Schematic of a) showing reciprocal lattice unit mesh and multiple (00) beams due to phthalocyanine crystallites.
c) LEED pattern near normal incidence for a multilayer deposit of metal-free phthalocyanine on Cu(111). Incident energy 14eV.
d) Schematic of c) showing two domains of the surface reciprocal unit mesh and the multiple (00) beams arising from these crystallites.
e) LEED pattern near normal incidence for a multilayer deposit of Fe-phthalocyanine on Cu(111). Incident electron energy 15eV.
f) Schematic of e) showing two domains of the surface reciprocal unit mesh and the multiple (00) beams arising from these crystallites.
References


7. See, for example, S. Andersson, I. Marklund and J. Martinson, Surface Sci., 12, 269 (1968).


Fig. 1

- Carbon
- Nitrogen
- Central "Metal" atom (Cu, Fe, H₂)

XBL.765-1666
Fig. 2
Fig. 4
Fig. 11
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