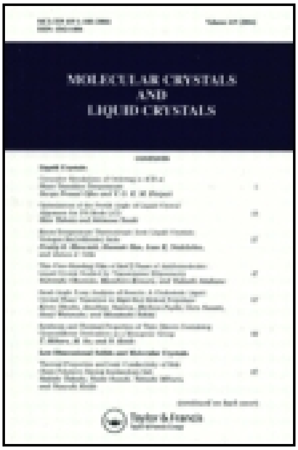

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# Simulation of Rheed Patterns of Ordered Organic Thin Films

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# SIMULATION OF RHEED PATTERNS OF ORDERED ORGANIC THIN FILMS

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**Abstract:** In the field of Organic Molecular Beam Epitaxy (OMBE), *in-situ* electron diffraction (RHEED) has become more and more common for structure analysis. A simulation method for RHEED patterns is described which pays special attention to electron diffraction on organic lattices. The calculation is based on the common diffraction theory in the kinematic approximation. Here we discuss first results of the theoretical simulation. The simulated patterns are compared to experimental results obtained on the system copper-phthalocyanine/Au(111). It is shown that even with the relatively simple assumptions made in the kinematic theory a good agreement between measured and calculated patterns is obtained.

## INTRODUCTION

Recently, there has been a large increase in the demand for well-ordered low-dimensional organic solids as a prerequisite for realising molecular devices like molecular wires, fast molecular switches and all kinds of organic-based sensors. One approach to produce thin ordered films of organic molecules is *Organic Molecular Beam Epitaxy* (OMBE) using highly stable molecules like phthalocyanines[1-3] or perylene derivatives[4,5]. The reliable characterisation of the physical structure of the layers achieved is very important. Besides real-space imaging techniques like *Scanning Probe Microscopy* or *Electron Microscopy* and related methods, a variety of diffraction methods leading to information about the reciprocal space are widely used. The most important of these are *Reflection High-Energy Electron Diffraction* (RHEED) and *Low Energy Electron Diffraction* (LEED). While LEED does not allow an real *in situ* investigation because of the geometry, RHEED can be directly employed to control the growth progress.

Since the first OMBE with *in situ* RHEED during actual film growth of copper-phthalocyanine (CuPc) monolayers on $MoS_2$[3] was performed, this method has become more and more common for the structural analysis of organic solids[1,6-8]. Interestingly, in most cases no irradiation damage occurs. Obviously, the inelastic scattering of electrons plays only a minor role. However, depending on the subtrate-deposit combination, sometimes a fast destructive process during irradiation has been reported[8].

In some cases, the simple "hand-made" analysis of the measured RHEED patterns results in sufficient information about the reciprocal lattice of the organic layer. However, if the structure is fairly complicated and no additional information is available, it is very difficult to construct a possible unit cell from that limited data obtained from the RHEED patterns. Furthermore, so far little attention has been paid to the influence of the internal structure of the molecule on the RHEED data itself, commonly treating the molecules as structure- and dimension-less lattice points. Therefore, the main goal of our simulation is to determine if a certain proposed structure *could* lead to the obtained RHEED pattern, thereby distinguishing between possible and impossible structures. Furthermore, we are interested in simulations of diffraction experiments on the computer with different molecules or even only with segments of a given molecule in order to get a better understanding of which parts of an organic molecule contribute most to the RHEED pattern observed.

Here we describe a simulation method for RHEED patterns with emphasis electron diffraction at organic lattices. The calculation is based on the common diffraction theory in the kinematic approximation. First results of the simulation are discussed and the calculated patterns are compared to our own experimental results.

## THEORY

### Diffraction method (short: *hkl*-method):

The basis of all electron diffraction theories is the consideration of the electron as a wave with a de-Broglie wavelength. In the kinematic theory only elastic scattering of the electrons at the lattice points is allowed; inelastic scattering as well as multiple elastic scattering are not regarded[9,10], i.e., the wavelength remains unchanged. Consequently, so-called forbidden reflexes cannot be modelled with the method presented here.

Using the well-known diffraction theory, developed by von Laue[9], the intensity of the scattered wave is calculated by superposition of the elementary waves and summation over the entire crystal or the coherence area. Without going further into the details we can state that - within the assumptions made above - the diffraction theory permits the calculation of the position, the shape and the intensity of the reflexes for ideal crystals. The attenuation of the intensity due to the absorption of the electromagnetic waves, caused by inelastic scattering, is not accounted for.

In our calculations we also take into account the energy distribution in the incoming electron beam by superpositioning waves of different wavelengths. Even if the wavelength variations are rather small (typically 0.1..0.01 %) an influence on the calculated images can be seen.

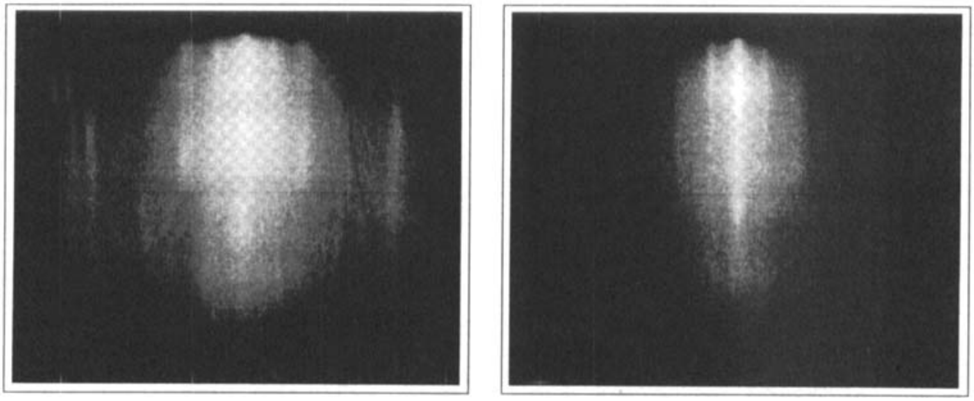
### Treatment of organic molecules and crystals:

To consider the internal structure of the molecules we use the complete molecule as the lattice basis, building together with the lattice (spanned up by the molecule centres) the physical structure. Then the structure amplitude for the entire unit cell is calculated, considering the different scattering efficiencies of different atom types. The atom coordinates of the atoms in the molecules are taken from an energy minimised structure, calculated with the program ALCHEMY III.

Generally, organic lattices with a symmetry different (lower) to those of the inorganic substrates allow several crystal domains. This has a strong influence on the RHEED diagrams if one turns the sample around in order to investigate several azimuths. Therefore, our algorithm allows us to calculate the RHEED patterns of different azimuths simultaneously.

## RESULTS AND DISCUSSION

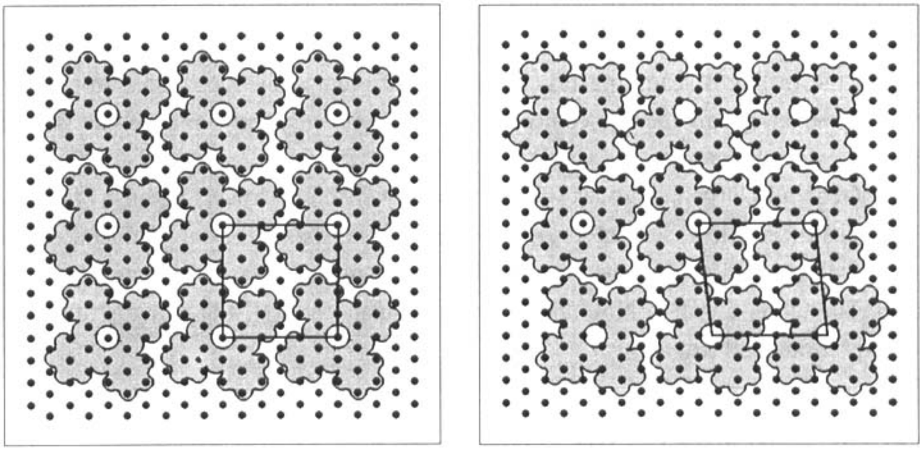
To demonstrate basic features of the RHEED simulation we compare the calculated patterns with measured data, obtained from a monolayer of copper-phthalocyanine on a Au(111)-surface produced by means of OMBE as described elsewhere[1] (Fig. 1). The very sharp and narrow streaks originate from the CuPc monolayer, while the wider streaks in the $\left[\bar{1}10\right]$-pattern stem from the gold substrate.



a) $\left[\bar{1}10\right]$-azimuth b) $\left[\bar{2}11\right]$-azimuth

**FIGURE 1** Experimental RHEED patterns of a CuPc overlayer on Au(111)

From STM-investigations[1] it is deduced that the CuPc layer exhibits a nearly square lattice with a lattice constant of 14.5±1.5 Å and a lattice angle of 90±6 degree. Our investigations did not reveal any information about the *c*-axis. Therefore, we assumed an orientation and length similar to that of the α-modification of CuPc[11]. Taking into account the error bars, two slightly different commensurable structures (Fig. 2) can be proposed the are not distinguishable by the STM data alone.

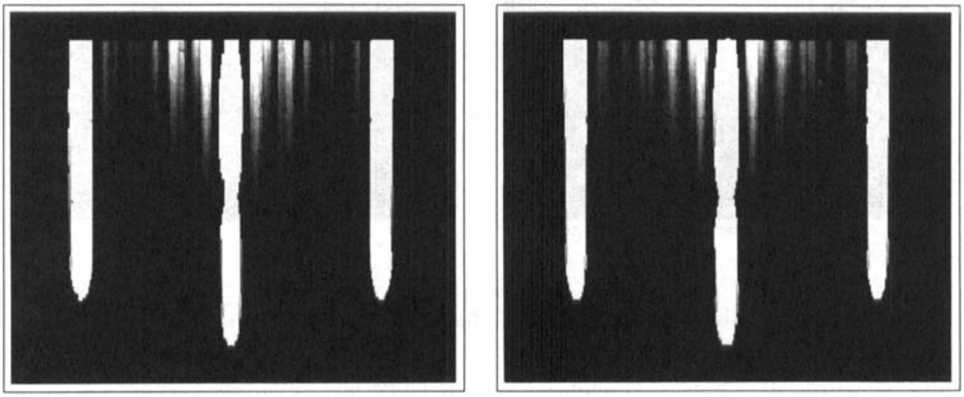


a) $a = 15.0$ Å, $b = 14.4$ Å, $c = 3.8$ Å
$\alpha = 64.5°$, $\beta = 96.6°$, $\gamma = 90°$,
$\delta = 30°$

b) $a = 15.0$ Å, $b = 14.5$ Å, $c = 3.8$ Å
$\alpha = 65.1°$, $\beta = 107.85°$, $\gamma = 96.6°$,
$\delta = 35°$

**FIGURE 2** Two possible structures for the CuPc overlayer

In the simulation, the scattering volume for the deposit was set to 3x3x1 lattice periods in *a*-, *b*- and *c*-directions, respectively. In order to obtain roughly the same dimensions for the substrate, the scattering volume was set to 15x15x2 (cubic unit cell). Here we chose a small thickness because the lack of absorption simulation would otherwise lead to wrong patterns. In all the simulations three domains for the deposit (separated by an

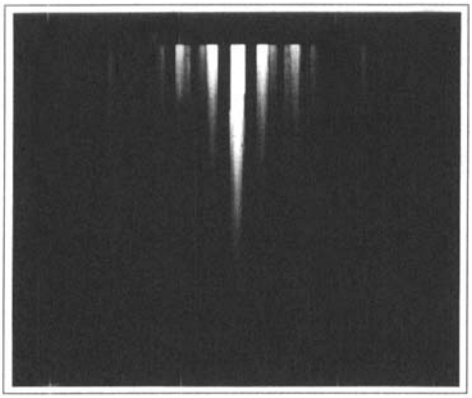


a) $[\bar{1}10]$-azimuth (to Fig. 2a)

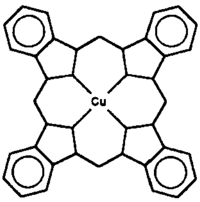
b) $[\bar{1}10]$-azimuth (to Fig. 2b)

**FIGURE 3** Calculated RHEED patterns of a CuPc overlayer on Au(111) angle of $120^0$) and two for the gold substrate (separated by $180^0$) were used. The latter is necessary because in different gold domains a different stacking order may occur. The primary beam had an energy of 10 keV and touched the surface at an angle of $1.5^0$ to the substrate plane. The viewing angle was $3.5^0$.

Our calculations (Fig. 3) reveal that a good agreement between experimental data and calculated patterns exists only for the structure proposed in Fig. 2a. In the other case the simulated pattern show a different characteristics: instead of a rather strong second streak, split up in two substreaks due to the (small) difference between the lattice constants *a* and *b*, a single second streak is found. It should be noted that the good agreement in the first case can be only obtained if three domains are regarded.



a) complete CuPc-molecules



copper-phthalocyanine (CuPc)

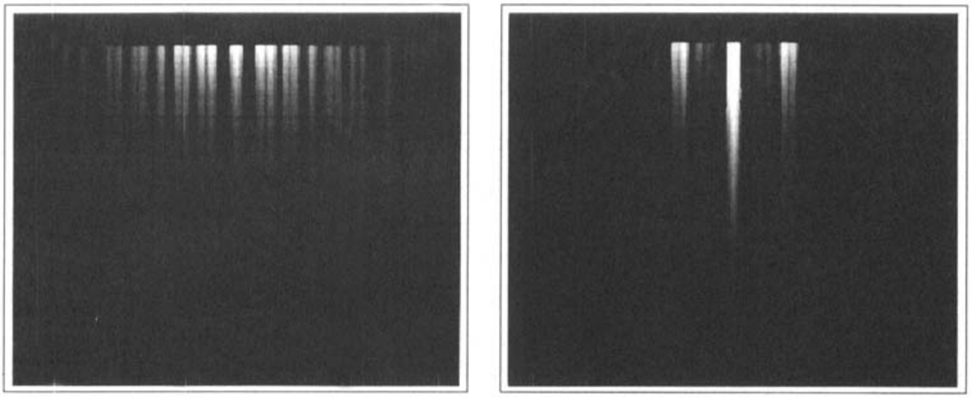


**FIGURE 4** Calculated RHEED patterns for different models of the overlayer

As a second example we calculated the RHEED patterns for the structure from Fig. 2a for different "approximations" for the CuPc-molecule: First, as in the previous example, we regarded the entire molecule (Fig. 4a). Then, we used the point approximation (a Cu-atom, situated at the site of the molecule, Fig. 4b). Finally, we ignored all but the four benzol rings in the CuPc molecule (Fig. 4c). For the sake of easier comparison the substrate reflexes are omitted in all three pictures.

The simulation results for the $[\bar{1}10]$-azimuth (Fig. 4) and comparison with the experimental findings (Fig. 1) indicate clearly that the intramolecular structure has a strong influence on the observed RHEED patterns. The point approximation does not lead to a sufficient explanation of the RHEED patterns observed in the experiment: although the streak distances are similar for the cases a) and b), the intensity distribution, especially the observed splitting of only the second reflexes, is not modelled correctly. On the other hand, completely different results are obtained if only the four benzol rings as the main part of the phthalocyanine molecule are considered: being separated on the substrate by a distance of approximately 7.5 Å, the resulting main streak distance in the RHEED diagrams is nearly twice that one of the complete CuPc. Again, all splitting of streaks into doublets is caused by the arrangement consisting of three different domains.

As a last example we wanted to investigate the influence of the layer thickness, a parameter which is difficult to measure in a real OMBE experiment with deposition rates in the order of only a few Å per hour. In addition to a monolayer of CuPc we calculated the RHEED patterns for 2 and 3 monolayers of CuPc on gold (111)-surfaces (images are not shown here). From the distinguishable spotty structure in the pattern of the 3 layer thick film, the much shorter reflexes and the change in the intensity distribution, we can conclude that our experimental data in Fig. 1 represent a very thin film of 1 or 2 monolayers of CuPc only.

## CONCLUSIONS

RHEED simulation is a helpful tool for analysing experimental data, as it allows one not only to distinguish between possible and impossible lattice structures but also leads to a better understanding of electron diffraction experiments. For the first time, a theoretical consideration of the whole molecule is made. The proposed simulation method reveals clearly that the influence of the intermolecular structure cannot be generally neglected. It is shown that even with the relatively simple assumptions made in the kinematic theory, a good agreement between measured and calculated RHEED patterns is obtained: the simulated diagrams show all the important features of the measured patterns, except of the diffuse intensity ("amorphous background"). The simulation of the intensity profile needs further improvement.

## ACKNOWLEDGEMENT

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