Origin of the anomalous X-ray diffraction in phthalocyanine films

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Abstract – The impact of the submolecular electron density on the X-ray diffraction profile
of a layer-stacked thin film is studied experimentally and compared with numerical simulations
based on the molecular structure and angular arrangement. Important structural information
is contained in the X-ray diffraction profile of highly anisotropic molecular thin films, such
as phthalocyanines. The results show that the intensity distribution of the diffraction peaks
belonging to the same series of lattice planes provides important structural information including
the molecular tilt angle and the center electron density of the molecule.

Introduction. – The electronic, optical, mechanical and other properties of solids depend critically and delicately on their physical and chemical arrangement of atoms [1]. Diffraction (X-ray, neutron, electrons) is a well-established method for the determination of the structure of solids and thin films. While the absolute X-ray diffraction (XRD) intensity is proportional to the square of the atomic index Z, generally the peak ratio of intensities of higher-order diffraction lines is independent of the Z number for a fixed structure; *i.e.* it is only determined by form factors, arising from the unit cell structure and the lattice configuration. Due to the complex molecular structure of metallo-organic solids it is customary in first approximation to model the structure of thin films based on the heavier metal ions neglecting the lighter organic atoms of the structure, or by introducing simple line shapes to simulate the contribution from the organic part [2–4]. We demonstrate here that including the organic ring is essential in diffraction studies of certain classes of organic solids, and of phthalocyanines in particular. Indeed, the diffraction by the organic portion of the molecules gives rise to unusual dependencies as a function of the Z-number of the metal ion. The diffraction peak ratios depend on the orientation of the molecules with respect to the substrates. This allows discrimination between various polymorphs of a molecule, which, in turn, has important consequences for the electronic and optical properties of thin films.

The macromolecular structure is routinely reconstructed from single crystal or powder X-ray diffraction data using a refinement procedure [5,6]. Usually, the important phase information is lost in the ordinary diffraction experiment, although there are exceptions for specific experimental conditions [7,8]. Classical techniques to retrieve phase information include molecular replacement [9], isomorphous replacement [10], and anomalous scattering [11], which perturb the diffraction pattern physically or chemically in order to partially deduce phase information. For monolayers, it is also feasible to measure the molecular tilt angle using Brewster angle microscopy [12,13]. However, for multilayered thin films, the experimental data obtained from such methods is incomplete and cannot recover the full molecular structure. Furthermore, off-specular diffraction profiles yield only very limited information, such as in-plane coherence length due to the polycrystalline nature of most organic thin films. In this case, the precise submolecular structure of anisotropic molecules in thin films is commonly ignored [3,4,14]. Even so the destructive interference of large, anisotropic molecules profoundly impacts the XRD intensities of higher-order diffraction peaks. This allows inferring molecular orientations (tilt angles) and discriminating between different polymorphs using the high-angle X-ray diffraction data shown here.

A key class of organic solids, such as quaterthiophene (4T), 3, 4, 9, 10 perylenetetracarboxylic dianhydride (PTCDA), 4-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST), and others [15–17], are constructed
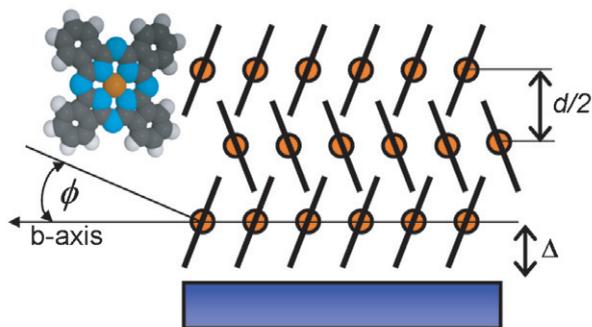

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Fig. 1: The definitions of the tilt angle (ϕ), the substrate gap (Δ) and the d-spacing of phthalocyanine (d) in a lattice of the α phase. For the β phase, the herringbone plane is parallel to the substrate surface. Circles represent the metal center and lines correspond to a side view of the nitrogen- and carbon-based molecule. The frontal view of a single copper phthalocyanine molecule $(CuC_{32}N_8H_{16})$ is shown at the top left.

from highly anisotropic molecules and form layered structures at the same time. Here, we illustrate this submolecular data extraction procedure for the case of thin films made of anisotropic organic molecules belonging to the phthalocyanine $(C_{32}N_8H_{16})$ family. The phthalocyanines are a subfamily of planar organic molecules, in which the center atom can be substituted with light or heavy metal atoms. The two most important structures in bulk and in thin films are the α and β phases [18,19]. Both are stacked in a so-called herringbone structure, while they differ in the tilt angle ϕ, see fig. 1. This molecule family is an ideal archetype for this study, because the electron density is significantly modified by substituting the center metal ion or by changing the tilt angle independently.

Experiment. – Advances in deposition methods with organic molecular beam epitaxy (OMBE) have led to high-quality, well-ordered thin films with interesting properties [20,21]. The phthalocyanine source materials were purified 3 times with the thermal gradient method under vacuum of less than 10^{-5} torr. About 20 to 30 monolayers (26 nm to 39 nm) thick metal-free phthalocyanine (H_2Pc) and copper phthalocyanine (CuPc) thin films were deposited on sapphire substrates in an OMBE system. The substrates were cleaned in an ultrasonic bath with acetone, isopropanol, and methanol to remove impurities. Phthalocyanine thin films in the α phase are deposited by sublimation at rates of about 0.5 Å/s in vacuum of better than 10^{-8} torr. The tilt angle ϕ is 26° for the α phase, see fig. 1. XRD profiles were measured for ten samples using a high-resolution Bruker D8 Discover system that has a fixed incident radiation energy with wavelength $\lambda = 1.54$ Å. Figure 2 shows typical XRD profiles for H_2Pc and CuPc thin films. Although CuPc and H_2Pc thin films have very similar d-spacings, the higher-order peak intensities differ significantly. Namely, the even-order diffraction peaks of the CuPc samples are significantly lower than those of H_2Pc thin films. The intensities of the
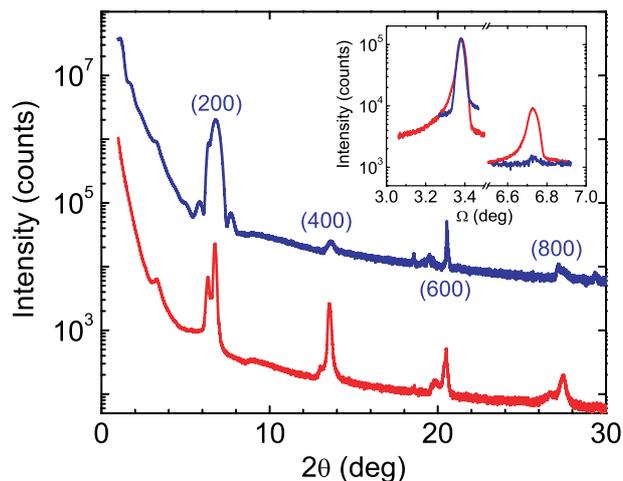

Fig. 2: Experimental θ-2θ XRD profiles of OMBE-grown α-H_2Pc (bottom) and α-CuPc (top) thin films on sapphire substrates. The CuPc is 36 nm thick and was grown with the substrate temperature at 150 °C. The curve of CuPc is shifted vertically for clarity. The CuPc (400) and (800) peaks are suppressed due to the interference of the phthalocyanine ring and the center Cu ion. If the metal center is substituted by H_2, then the (400) and (800) peaks are not suppressed. Inset: rocking curves of the first- and second-order diffraction peaks for CuPc and H_2Pc.

first- and second-order Pc peaks were obtained from the maximum height of rocking curves to avoid misalignment. The peak ratio is defined as the intensity ratio of the first two peaks. The small peaks at 3.3°, 6.6° and higher orders are background contributions.

Discussion. – Previous quantitative structural studies of phthalocyanine (Pc) thin films focus on the interlayer structural parameters such as the d-spacing, film roughness, and strain while assuming either a step-function [2], Gaussian [3], or sinusoidal [4], electron density profile within a monolayer. In such cases, the heavy central atom is assumed to dominate, while the contribution from the surrounding organic part is considered to be an additional smaller electron contribution. Here, the exact structural factor $f^{Pc}(Q)$ is calculated using the well-known positions of all 57 atoms of the metallo-phthalocyanine molecule [22] and angle-dependent scattering factors for each element calculated with the 9-parameter Cromer-Mann equation [23]. The wave vector Q is perpendicular to the substrate plane and depends on the scattering angle θ as $Q = (4\pi/\lambda)\sin(\theta)$. Since the phthalocyanine ring deforms insignificantly from the plane when the center pair of hydrogen atoms is replaced by a metal atom (except for heavy atoms above Ba) [22,24], a rigid phthalocyanine ring with fourfold symmetry is used in the calculations. The resulting electron density of anisotropic molecules along the stacking direction shows a complex fine structure that depends on the molecular anisotropy and the molecular tilt angle. In addition to the center maximum of the electron density, several local maxima appear that depend on

the tilt angle ϕ and the type of metallo-phthalocyanine. In the following, the role of the center atom and the angular arrangement of the molecule are discussed, while keeping the contribution from the interlayer structure fixed.

To understand the effect of the center atom on the diffraction profile of a phthalocyanine thin film, we propose a quasi–one-dimensional model, which includes the essential features of the phthalocyanine film. In other words, the lateral structures such as the in-plane texture, the lateral grain size and the angular uniaxial distribution along the stacking direction, generally labeled as $(h00)$-direction for the α phase or $(00l)$-direction for the β phase are not considered. But the three-dimensional features of the structure factor for phthalocyanines are included. Since the lattice constants for H_2Pc and metallo-phthalocyanine are very close, it is reasonable to choose a model in which only the central atom is varied and the remaining intermolecular structure is fixed [18]. We assume structural coherence (*i.e.* ignoring diffuse scattering due to thermal vibration and in-plane continuous deformation) and that the surface roughness of phthalocyanine thin films is uncorrelated and the diffraction intensity from the film with a contribution from a substrate can be written as

$$I(Q) = A(\theta)\Big\langle F^*(Q)e^{-i\Delta \cdot Q} + F^{\text{Sub}^*}(Q)\Big\rangle$$
$$\cdot \Big\langle F(Q)e^{i\Delta \cdot Q} + F^{\text{Sub}}(Q)\Big\rangle,$$

in which $F(Q)$ and $F^{\text{Sub}}(Q)$ are the scattering factors of the phthalocyanine film and the substrate. The gap between the substrate and the center of the first monolayer is given by Δ. The substrate contribution is integrated using the attenuation μ and the electron density $\rho(z)$ of sapphire: $F^{\text{Sub}}(Q) = \int_{-\infty}^{0} \rho(z)e^{-\mu z/2}e^{iQz}\mathrm{d}z$. The scattering factor $F(Q)$ is obtained by summing $f^{\text{Pc}}(Q)$ over a unit cell and integration over 20 monolayers. The number of monolayers is fixed, the total film thickness may vary depending on the tilt angle and the structural phase of the organic thin film. The roughness of the uncorrelated stepped surface is included and taken to be 10% [3]. Lastly, an instrumental correction is represented by an angular dependent coefficient $A(\theta)$. For the calculations, we have included the Lorentz factor, polarization, and a projection correction in this coefficient. Note that for intensity ratios at a fixed angle, this angular dependent coefficient cancels out. Then assuming that the substrate-film gap is half the thickness of the phthalocyanine monolayer ($\Delta = 6.5\,\text{Å}$), the line profile can be calculated numerically and maximum intensities of the first ($2\theta \approx 6.8°$) and second ($\approx 13.6°$) order diffraction peaks are extracted as a function of the atomic index of the center atom for α and β forms, see fig. 3. Empirically, the intensity of the first peak increases exponentially with Z, the number of electrons. However, the falling trend of the intensity of the second-order peak is unexpected. This anomalous decrease is related to the destructive interference of the
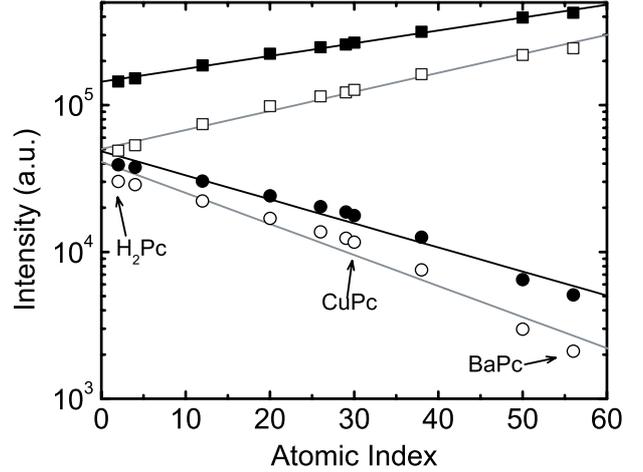

Fig. 3: Calculated intensity of the first (square) and second (circle) order diffraction peaks as a function of the atomic index of the center atom from H_2 to Ba in the α (solid) and β (hollow) phases. Lines are linear fits to the calculated data.
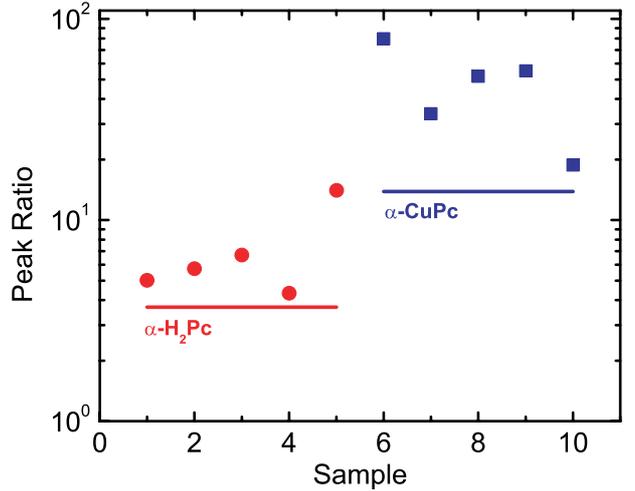

Fig. 4: Experimental and calculated intensity ratio of the first-to second-order diffraction peak. Squares and circles correspond to experimental data of 5 samples for H_2Pc and CuPc, respectively. Lines are the calculated values for H_2Pc and CuPc, respectively.

complex structure factor of an anisotropic molecule. Plotting the ratio of the first- and second-order peaks for several deposited thin-film samples we find indeed that the experimental data (circles, squares) confirms what we expect from the calculation of the α phase (straight lines) shown in fig. 4. The calculated values have no fitting parameters, and do not take disorder (continuous roughness) into account. Such disorder contributes less to the intensity for higher scattering angles. Therefore, the experimental ratios are slightly higher than the calculated values. Clearly, for a fixed tilt angle, the XRD peak ratio is an indication of the center electron density.

In addition to the center atom substitution, the tilt angle of the phthalocyanine molecule may change [25–27].
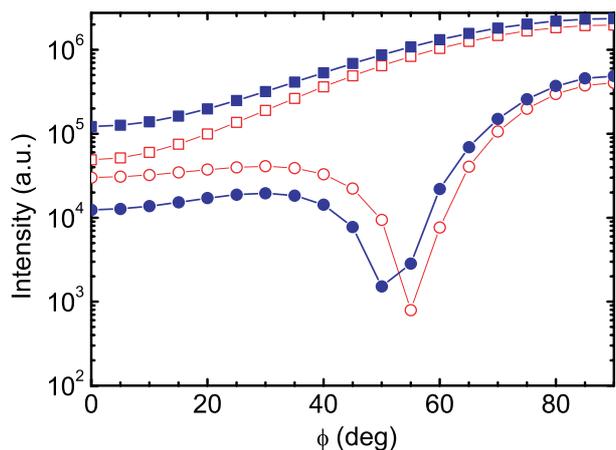
Fig. 5: Calculated intensity of the first (square) and second (circle) order peaks for H_2Pc (open) and CuPc (solid) thin films as a function of the molecular tilt angle ϕ. The tilt angle can be inferred from the strongly ϕ-dependent peak ratio.

This produces a change of electron density along the stacking direction. Although the molecules in a phthalocyanine thin film cannot be inclined arbitrarily, since only a few angles correspond to stable or metastable configurations, the relation of the XRD profiles as a function of the tilt angle can still be studied numerically. The tilt angle dependence for H_2Pc and CuPc thin films on sapphire substrates is shown in fig. 5. The intensity of the first-order peak increases monotonically with the tilt angle ϕ for both CuPc and H_2Pc. However, the intensity for H_2Pc increases faster with the tilt angle and approaches that of CuPc at $\phi = 90°$ (the molecule lies flat on the substrate). The intensity of the second-order peak is not monotonic and shows a minimum near $\phi = 50°$, at which point the scattering factors of the organic atoms and the center atom interfere destructively. Note that the peak intensity ratio of CuPc is more than 6 times larger than the ratio for H_2Pc at $\phi = 0°$. This fraction of ratios decreases for larger inclinations (except near $\phi = 50°$) and becomes unity at $\phi = 90°$. Thus, in an ordered film, the peak ratio between the first- and second-order peaks is characteristic of the tilt angle of the molecule. In the special case of $\phi = 90°$, the approximation that the entire electron density can be concentrated in a single point at the center holds true and the molecule can be treated as an isotropic particle without internal structure. The (600) and (800) CuPc peaks in fig. 2 contain the same information as the (200) and (400) peaks, but were not specifically discussed due to their experimentally lower intensity.

We have investigated other possible origins for this strong intensity dependence mentioned above. In fact, the different magnitude of the peak ratio can also be the consequence of destructive interference of the structure factor between the phthalocyanine thin film and the substrate. However, an analysis shows that the contribution from the substrate is much smaller and does not exceed 20% of the intensity ratio. We conclude that the dominating contribution to the peak ratio is the tilt angle for a fixed center atom.

Conclusions. – In summary, we have studied the effect of the submolecular structure of highly anisotropic molecules on X-ray diffraction. The X-ray diffraction profile contains important information on the submolecular electron density distribution and angular arrangement of the molecule due to interference of light and heavy atoms in the molecule. This is illustrated for two anisotropic, planar phthalocyanine molecules that differ only by the central atom. The subtle difference in the electron density profile can greatly impact the X-ray diffraction line profile of two major peak intensities. The destructive interference between the central metal atom and the surrounding organic rings of the molecule is an essential part of the diffraction profile for layer-stacked organic thin films. This leads to an anomalous decrease in even-order peak intensities with heavier center atoms in the molecule. Without the inclusion of the surrounding organic rings, the ratio of the first- and second-order diffraction peaks is constant for all compounds of the phthalocyanine family. The experimental data confirms the interplay of the heavy electron center with the lighter carbon- and nitrogen-based rings as evidenced in the big difference of peak ratios between H_2Pc and CuPc. The tilt angle of anisotropic molecular based thin films is also determined from the XRD profile. For phthalocyanines, the complex structure factor interferes destructively near 50°, which results in a maximum peak ratio between the first- and second-order diffraction peaks. Although using the average electron density profile works successfully with limited ordered systems, such as the smectic liquid crystal [28], a careful analysis is required for highly ordered OMBE-deposited thin films. Consequently, it is found that the first to second peak ratio provides i) the center electron density of the molecule, and ii) the tilt angle of the anisotropic molecule.

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