Quantifying and enforcing the two-dimensional symmetry of scanning probe microscopy images of periodic objects

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Abstract

The overall performance and correctness of the calibration of all kinds of traditional scanning probe microscopes can be assessed in a fully quantitative way by means of "crystallographic processing" of their two-dimensional images from samples with periodic features. This is because crystallographic image processing results in two residual indices that quantify by how much the symmetry in a scanning probe microscopy image deviates from the symmetries of each of the plane groups. When a likely plane group has been identified on the basis of crystallographic image processing, the symmetry elements in the scanning probe microscopy image can be enforced in order to obtain "clearer" images of periodic objects, effectively removing the less than ideal "influence" of the microscope on the imaging processes. This paper discusses the crystallographic image processing procedure for a scanning tunneling microscopy image of a mono-layer of fluorinated cobalt phthalocyanine on graphite.

Keywords: scanning probe microscopy, quantification, two-dimensional symmetry

Introduction

Many different kinds of scanning probe microscopes (SPM) have been developed since the inventions of the scanning tunneling microscope (STM) and the atomic force microscope (AFM) in the early 1980s. The defining features of this type of microscope are a very fine probe that is scanned laterally in two dimensions (2D), in very fine steps, very close to the surface of a sample (while being controlled by a feedback mechanism) and a probe-sample interactions signal that is recorded at each scanning increment.

This signal can then be digitized and prepared for its displays as function of the magnified scanning steps. Between the scanning steps, the signal may be interpolated to provide for a smooth display. The digitized signal can, for example, be converted by a certain code into colors for a pseudo three-dimensional perspective false-color display of the probe-sample interactions. Traditional SPMs produce only single valued surface topography and probe-sample interaction maps so that the "shapes" of the imaged objects are only a subset of all possible three-dimensional shapes [1].

To a reasonably good approximation, a 2D-image of the probe-sample interactions as recorded in a traditional SPM can be obtained by simply ascribing the digitized signal directly to its respective scanning increments in 2D. This image corresponds then to an orthogonal projection of the signal from the third dimension (z-direction) of the sample on to the 2D scanning (x-y plane) plane. (Note that while this is strictly true only for pure constant-tunneling-current images, it is a rather good approximation for the images of most traditional SPMs.) Like any other 2D image, these images can be subjected to image processing routines in order to quantify the information contained in them. A proper calibration of the whole microscope is essential for the quantification of this kind of information. The calibration of a SPM may be assessed by the use of calibration standards, e.g. ref. [2].

For SPM images from periodic objects, crystallographic image processing (CIP) [3] can be used to quantify the 2D symmetry [4] in the images. Utilizing calibration standards with known periodic features and CIP allows for a fully quantitative assessment of the overall performance and correctness of the calibration of a SPM. This will be discussed at the end of this paper.

Basics and procedure of Crystallographic Image Processing

CIP is widely employed in electron crystallography to aid the extraction of structure factors from high-resolution phase contrast images that are recorded at transmission electron microscopes [5,6]. The underlying 2D symmetry quantification principles of CIP are, however, completely general. This is because there are just 17 symmetry groups for periodic objects in 2D [7]. (To aid the discerning of the orientation of mirror and glide lines, 21 plane group symbols [7] are used in this paper and the CIP software [3]). The amplitude (F) and phase (a) of the Fourier coefficients of the intensity of any image have to obey certain symmetry relations and restrictions in order to belong to one of these plane groups [6,8]. The amplitude and phase residuals of the Fourier coefficients of a 2D-image will be different for each of the plane groups and provide, therefore, a means to quantify symmetry in 2D.

Note that both of these residuals would be zero for an exact adherence of an image to one of the plane groups. This would correspond to a measurement without any systematic and random errors. The amplitude (F_{res}) and phase (a_{res}) residuals are defined by the relations [6]:

$$F_{res} = \frac{\sum_{HK} |F_{obs}(H,K)| - |F_{sym}(H,K)|}{\sum_{HK} |F_{obs}(H,K)|} \quad \textit{in percent and}$$

$$a_{res} = \frac{\sum_{HK} w(H,K) \cdot |a_{obs}(H,K) - a_{sym}(H,K)|}{\sum_{HK} w(H,K)} \quad \textit{in degrees}, \text{ where}$$

the subscripts stand for observed and symmetrized, *w* is a relative weight, and the sums are taken over all Fourier transform coefficient labels *H* and *K*.

Note that critical dimension SPMs can record images with shapes that are not revealed by traditional SPMs [1]. The 80 diperiodic space groups [9] are the basis for quantifications of the symmetry of those images.

Quantifying and enforcing 2D plane symmetry on STM images of a mono-layer of F_{16}CoPc on graphite

STM images have been recorded at 20 K from a mono-layer of fluorinated cobalt phthalocyanine (F_{16}CoPc) on highly (0001) oriented pyrolytic graphite [10]. Graphite possesses space group $P6_3mc$ (No. 186) and the plane group of its (0001) surface is p6mm. Silver [11] and gold [12] (both possessing space group $Fm\bar{3}m$, No. 225) in the (111) orientation are also popular substrates with the p6mm symmetry for mono- and multi-layers of tin phthalocyanine (SnPc) [11] and cobalt phthalocyanine (CoPc) [12]. Other popular (0001 oriented) substrates with the same plane group for STM analyses of phthalocyanines are MoS_2 [13] and WSe_2 [10] (as both possess the space group $P6_3/mmc$, No. 194). High resolution transmission electron microscopy (HRTEM) studies, on the other hand, prefer (001) oriented KCl (with possesses plane group p4mm, space group No. 225) [14] as substrate, because it can be readily removed from the deposit by dissolving in water. The F_{16}CoPc molecule, Fig. 1, and all homologous phthalocyanines possess (in their planar projections) the 2D point symmetry group 4mm.

Following Curie's symmetry principle [15] (and disregarding the differences in the sizes of the 2D unit meshes and the underlying atomic near-surface structure, as well as possible preparation induced reconstructions, but assuming strong interactions between the deposit and substrate), one would expect that the epitaxial arrangement of a mono-layer of F_{16}CoPc on all of the "p6mm substrates" is either p2, p1m1 (= pm, m ⊥ x, meaning that the mirror line is perpendicular to the vertical axis of the unit mesh), or p11m (= pm m ⊥ y).

Free energy minimization between the deposit and substrates may result in higher or lower plane symmetries for these monolayers depending on the temperature. If the interaction energy between the deposit and the substrate is low in comparison to the energy of inter-molecule interactions, the mono-layer may possess plane symmetries as high as p4mm or p4.

From the viewpoint of the plane symmetry, the group p4mm can be realized for a metal phthalocyanine when two molecules (with point symmetry 4mm) "pair up" to form one motif of this plane group.

Such an effect and plane group p4mm have actually been observed experimentally for SnPc on Ag (111) [11]. Either identical or opposite sides of the individual molecules (that make up the pair) can thereby be in contact with the surface of the substrate. Such a "pairing up" of two molecules into one motif of the plane group p4mm is indicative of strong anisotropic inter-molecule interactions and results in a four-fold larger unit cell that p4. At high temperatures, the entropy term of the free energy may become large so that sub groups of p4mm or p4, i.e. c2mm, p2mm, p2, or p1 may be realized.

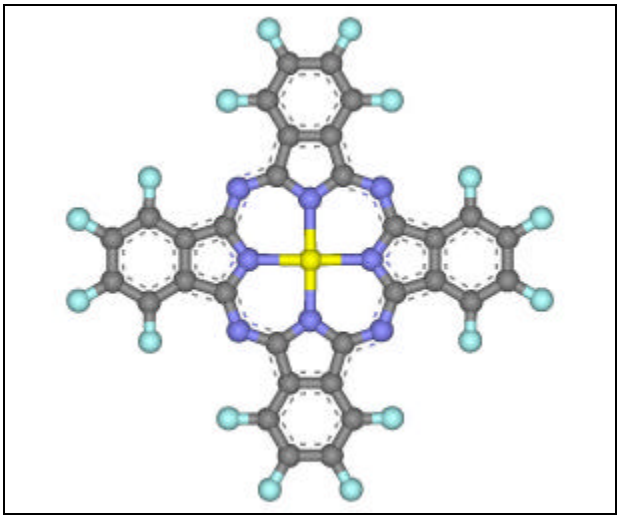

Fig. 1: Model of the structure of fluorinated cobalt phthalocyanine (F_{16}CoPc). The 2D point symmetry group of this molecule is 4mm. All other (homologous) phthalocyanines (where the central Co atom may be replaced by a transition metal atom of valence two, all of the F atoms may be replaced by other halogens or hydrogen atoms) possess the same point symmetry. Some of these molecules are flat, e.g. F_{16}CoPc or CuPc. Others have their central metal atom out of plane, e.g. SnPc [11] or PbPc.

From the 2D point group of the F_{16}CoPc molecule, it is, however, unlikely that the 5 plane groups that contain glide lines in oblique and rectangular 2D-lattices and the plane group p4gm will be realized for its mono-layers on the above mentioned substrates with plane symmetry p6mm. Following Curie's principle [15], the 5 plane groups with hexagonal lattices can also be excluded as possible symmetries of an F_{16}CoPc monolayer on substrates with the plane group p6mm.

The quantification of the plane symmetry of a mono-layer of F_{16}CoPc on graphite with the current (windows based) version of the program CRISP [3], Fig. 2, results in residual indices for the possible plane symmetries as given in Table 1. (Note that the data of this table are

actually from the table in Fig. 2.) Plane group c2mm has been excluded from table 1 because the Fourier transform of the raw STM image, Fig. 3, did not show systematic absences that were caused by the centering of a rectangular lattice*.

	p2	p1m1	p11m	p2mm	p4	p4mm
F_{res} [%]	-	15.4	15.4	15.4	27.0	28.3
a_{res} [°]	20.9	17.9	19.3	28.6	21.3	31.2

Table 1: Amplitude and phase residuals for possible plane groups of a mono-layer of F_{16}CoPc on graphite.

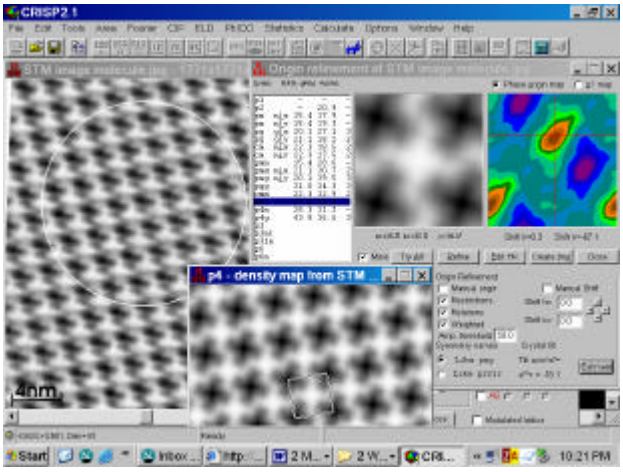

Fig. 2: Screen shot of CIP on a STM image of an F_{16}CoPc mono-layer on graphite. The plane group symmetry p4 is enforced in the so called "density map". The motive is arranged in a square lattice, while both sets of mirror lines of the point symmetry of the molecules are not realized in the plane symmetry.

It is possible that the molecules of the monolayer are not parallel to the substrate. In the absence of detailed free energy calculations, we conclude preliminarily from table 1 and Fig. 2 that p4 or p4mm are the probable plane groups for the arrangement of a mono-layer of F_{16}CoPc on graphite (and that the interaction energy between deposit and substrate is not high). This conclusion is based on the fact that the phase residual is not much higher for p4 than for p2. Similarly, the phase residual is not much higher for p4mm than for p2mm. (Note that p2 does not have an amplitude residual because $F(H,K) = F(-H,-K)$ is a property of the Fourier transform itself. From the difference in the phase residuals of the plane groups p2mm, p1m1 and p11m, one can conclude that the two mirror lines are not exactly perpendicular to each other.)

For comparison, the plane group p2 has been inferred by other authors from experimental STM data that were recorded at 78 K from a CoPc mono-layer on an (111) oriented Au substrate [12]. There was, however, no quantification of this symmetry so that this result remains open to discussion. The qualitative symmetry inference of these authors may have been affected simply by artifacts of their microscope's calibration.

Figure 3 shows raw STM data from a mono-layer of F_{16}CoPc on graphite as background and symmetry enforced versions of this data as insets. Because the signal in the z-direction is based on a quantum mechanical tunneling effect, STMs are much more sensitive in this direction than they are in any direction in the x-y plane. The enforcing of plane symmetries is applied to this plane only so that the total tunneling signal per unit area is not affected. Enforcing plane symmetries on STM images results, therefore, only in lateral shifts of "symmetry averaged" tunneling signals.

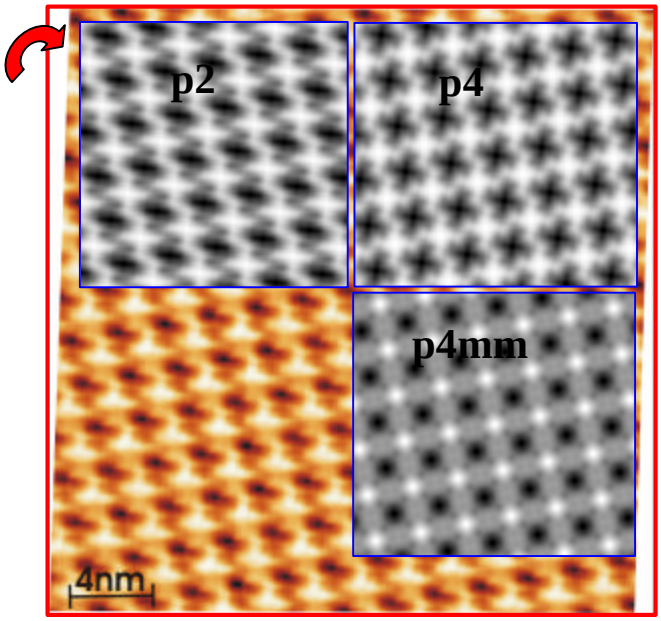

Fig. 3: STM images of an F_{16}CoPc mono-layer on graphite, raw data as background and in 3rd quadrant, symmetry enforced data with respective labels as insets. Note that compared to the symmetrized data, the raw data appear to be "clockwise twisted (see arrow), sheared, and anisotropically stretched". The motives of the p2 and p4 maps are rotated clockwise with respect to its counterpart in the p4mm map.

This leads us to another potential usage of CIP of SPM images. Provided that a calibration standard with known periodic features, i.e. known plane group for the whole sample and known point group of the periodic motive, is available, the overall performance and the correctness of the calibration of the SPM can be straightforwardly assessed. In these cases, the amplitude and phase residuals (such as given in Table 1) provide quantitative measures of the performance and calibration of the microscope.

As long as the symmetry of the calibration standard is high, e.g. plane group p4mm or even better p6mm, the amplitude and phase residuals for all of their subgroups can also be used as quantitative measures for the existence of certain combinations of symmetry elements. The combined effects of all kinds of deviations from a "perfect SPM", i.e. a probe shape that deviates significantly from point group infinity, excessive noise,

mis-calibrations of the x-y step sizes, and non-linearity can, thus, be detected in the experimental SPM data. Note that the whole procedure is quite similar to standard practices in HRTEM image-based electron crystallography [5,6]. For example, after the phase contrast transfer function of the electron microscope has been deconvoluted from the experimental image, the correct plane group of the projected electrostatic potential can be identified by its low phase and amplitude residuals. Note also that HRTEM studies of halogenated phthalocyanines revealed plane group p4mm [14] (in compliance with Curie's symmetry principle [15]). Imposing this plane symmetry removes the imperfections of the imaging process from the structural data of the molecules.

Summary and Conclusions

Symmetry is an abstract mathematical concept and has been said to lie in the "eye of the beholder" for real world objects such as 2D-images of the probe-sample interactions that are recorded by a SPM. Symmetry can, however, be quantified by crystallographic image processing. This quantification can be used to assess the overall performance and correctness of the calibration of all kinds of SPMs. Enforcing the correctly identified plane symmetry on a SPM image results in the effective removal of artifacts that are due to the microscopical imaging process.

Acknowledgments

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* The table in Fig. 2 actually shows as fifth column the so called Ao/Ae ratio for plane groups p1g1, p11g, c1m1, c11m, p2mg, p2gm, p2gg, c2mm, and p4g. All of these plane groups have "symmetry forbidden" Fourier coefficients, i.e. due to the presence of centerings and/or glide lines, the amplitudes of certain Fourier coefficients are supposed to be zero. The Ao/Ae ratio is defined as the amplitude sum of the reflections that are forbidden by the symmetry but were nevertheless observed (Ao) divided by the amplitude sum of the observed reflections (Ae) that are allowed by the plane symmetry.

A quantifying number of this ratio means that plane group forbidden Fourier transform components are actually present with a measurable amplitude in the Fourier transform of the experimental STM image, Fig. 2. Since the Ao/Ae ratios are relative measures of the "deviations of symmetry forbidden Fourier coefficients" for nine of the plane groups, they are additional measures to quantify symmetry for these plane groups. If any of these plane groups were to be identified, its Ao/Ae ratio needs to be close to zero. Because the Ao/Ae ratio is for all of these plane groups between 2 and 3, see table in Fig. 2, it is clear that the STM image is not compliant with any of the plane groups mentioned in this footnote.