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Crystal Structure and Molecular Orientation in Phthalocyanine Thin Films

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In a recent series of papers, Ashida *et al.*[1] investigated the crystal structures of several metal phthalocyanine thin films. Ashida obtained two types of films which he assumed had identical crystal structures but in different orientations. A comparison of Ashida's data with other published data (Honigman[2]) suggest that the structures in the two types of thin films may be different and have different space groups.

Ashida[1] has found that metal phthalocyanine thin films can be vacuum deposited on a Muscovite substrate in one of two ways: either with the crystallites parallel with the surface (fiber crystals) or with the crystallites standing obliquely to it. (Note, the latter orientation occurred on slightly cleaner muscovite surfaces.) In the case of copper phthalocyanine (CuPc) and platinum phthalocyanine (PtPc) the electron diffraction patterns could be interpreted in terms of the structures in Table 1. On the basis of the agreement between the dimensions that had been measured, Ashida assumed that the structures in the two orientations were identical. He considered that the differences in the angles might be the result of distortions by the substrate in the two orientations. By combining the possible reflections in the two sets of data, Ashida concludes that the crystal structures are monoclinic with A2/a space group.

Work by Honigmann suggests that Ashida's explanation may be incomplete. Honigmann reports on two metastable crystal structures of copper phthalocyanine which have been identified in

TABLE 1 Electron Diffraction Structures for Phthalocyanine Thin Films

Orientation	*a*	*b*	*c*	α	β	γ
CuPc parallel to substrate (Fiber crystals)	23.92	3.79	25.92	—	93.2	90
CuPc oblique to substrate	23.8	—	25.8	—	90.4	—
PtPc *b* axis parallel to substrate (Fiber crystals)	23.84	3.818	26.18	—	95.1	90
PtPc *b* axis oblique to substrate	23.8	—	26.2	—	91.9	—

the literature as gamma and alpha modifications.[3] By comparing X-ray powder patterns of known and unknown structures, Honigmann was able to characterize two separate crystal modifications for the copper phthalocyanine (Table 2). Although the lattice spacings of both forms are almost identical, the space group of the alpha structure was triclinic, not monoclinic. (A pseudo-monoclinic cell centered on the *a* and *c* axes can be defined as shown in Table 2.)

TABLE 2 Metastable Copper Phthalocyanines

Structure	*a*	*b*	*c*	α	β	γ	Space Group
"Gamma" (precipitated from 60% H_2SO_4 slurry)	24.0	3.8	26.2	90	93.9	90	A2/a
"Alpha" (precipitated from conc. H_2SO_4 slurry)	24.2	3.8	26.4	90	90.1	95.6	1 or $\bar{1}$

A comparison between Honigmann's data and Ashida's copper phthalocyanine thin film data suggests that Ashida had not one but two crystal structures. Ashida's crystals, oblique to substrate, give a diffraction pattern corresponding to Honigmann's triclinic ("alpha") form. A comparison of dimensions indicate that Ashida fiber crystals are identical to Honigmann's monoclinic "gamma" structure. In other words, the monoclinic structure, that Ashida assumed for the copper phthalocyanine crystals in both orientations may occur only in one: the fiber crystals; and a new triclinic structure occurs in the crystals oblique to the substrate. Ashida's data also indicates two different crystal structures for his platinum phthalocyanine films; the fiber crystals give identical results to those from Honigmann's monoclinic structures.

In both the copper and platinum phthalocyanine films, the crystals appear to transform from the monoclinic to triclinic structure as they reorient onto the cleaner muscovite surface. A possible explanation for both the structural transformation and crystal reorientation appears when we consider the orientation of the molecules with respect to the substrate in the various crystallites. Following Ashida's example we will determine first the orientation of the crystal axes to the substrate and then the orientation of the molecular axes to the substrate.

Using the cell dimensions (a, c, and β) as measured directly for the oblique orientation, and using the values for α and γ as determined by Honigmann, the orientation of the triclinic copper phthalocyanine crystals with the substrate may be determined. It is found that the a, b, and c axes make angles of 107°, 20° and 74° from the normal to the substrate. For the crystals of platinum phthalocyanine, a similar procedure indicates that the angles between the a, b, and c axes and the normal of the substrate are 116°, 22°, and 82° respectively.

Honigmann has shown that in chlorinated copper phthalocyanines the orientation of the molecules to the b and c axes are identical in both monoclinic and triclinic structures. Assuming this is the case for platinum phthalocyanine thin films with b axes oblique to the substrate, the molecular orientations with the *b* and *c* axes may be calculated from the structure determined by Robertson[4] (Table 3).

The correspondence between the last two columns indicates that the molecular planes are approximately flat on the surface. The similarity between the orientations to the substrate by both copper and platinum phthalocyanine crystals leads to the conclusion that a matching of molecular planes in with the substrate also occurs in triclinic crystals of copper phthalocyanines.

TABLE 3 Orientation of the Platinum Phthalocyanine Molecule in the Crystal

	Angles between molecular axes (*L*, *M*, *N*) and crystal axes			Angle between the triclinic crystal axes and substrate normal
	L	M	N[a]	
b-axis	85.7°	63.9°	26.5°	22°
c'-axis[b]	12.8°	103.5°	88°	82°

[a] Molecular axis *N* is the normal to the molecular plane. Molecular axes *L* and *M* are defined in reference 4.

[b] The *c'*-axis is defined from Robertson's by the transformation $c' = -2c - a$.

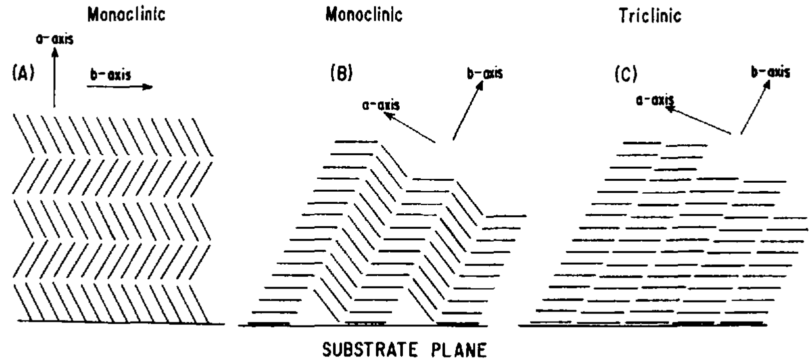

Figure 1.

Figure 1 compares, schematically, Ashida's results for the molecular orientations in the monoclinic structure for the two crystal orientations: fiber crystals, "A" and *b* axis standing crystals, "B". The orientation of molecules for the new triclinic structure for the latter crystals is shown in "C".

From Fig. 1 it is clear that the main result of the reorientation of the crystallites into the standing position is the matching of molecular and substrate planes. The energy gain by such a match would be maximized by switching the crystals from the monoclinic (B) to triclinic (C) structures. Since several other structural transformations are known to occur in the phthalocyanines with small energy change[3] it is possible that the structural transformation could occur between reoriented thin films. In conclusion, the number of known phthalocyanine structures has been increasing steadily over the last few years and it would seem that new structures will continue to be found as long as new environments can be used for crystal nucleation and growth.

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