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The Orientation Overgrowth of Metal-phthalocyanines on the Surface of Single Crystals. I. Vacuum-condensed Films on Muscovite

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When substrate muscovite is preliminarily heated at 300°C for one hour and then kept at 150°C to 200°C during deposition in vacuo, Cu-phthalocyanine films condensed on it show parallel b-axis orientations, including single- and triple-directional orientations. The b-axis of the crystal runs parallel to the substrate face. On the other hand, when the substrate is preliminarily heated at 400°C and then kept at 150°C, films vacuum-condensed on it occur in a standing b-axis orientation. The high-resolution electron-diffraction pattern of the film reveals that the a-, b- and c-axes of the crystal are inclined to the normal of the substrate face at angles of about 75°, 32° and 118° respectively. An electron micrograph of the film shows that as discrete crystals grow they orient themselves in either of two different directions. The crystal which assumes the standing b-axis orientation has its $(31\bar{3})$ plane almost parallel to the substrate face. Pt-phthalocyanine film also assumes the standing b-axis orientation, in which the a-, b- and c-axes of the crystal are inclined to the normal of the substrate face at angles of about 74°, 35° and 120° respectively. It turns out that the molecular plane comes in contact with the muscovite surface in the case of the standing b-axis orientation. A plausible explanation of the origin of these orientations is presented in terms of the dehyroxylation of the surface mica layer caused by the thermal treatment.

The epitaxial growth of thin crystalline film has been investigated by many workers; they have mostly been interested in metals or inorganic compounds. As for the organic compounds, Willems1) and Kleber and Meyer2) observed the orientation overgrowth of some compounds by light microscopy. However, the method based on light microscopy was limited to cases where the overgrown crystals have a well-defined morphology. Moreover, the lack of exact information on the crystal structures of most of those compounds made it impossible to discuss in detail the orientation of the crystals relative to the substrate in terms of a difinite lattice structure. In a previous paper,3) it was reported that the condensed polycyclic aromatic compounds, which are frequently referred to as the organic semiconductors, show an epitaxial growth when those materials are condensed onto a cleaved face of muscovite crystal. Furthermore, it was observed by electron microscopy and electron diffraction that platinum-, copper- and zinc-phthalocyanines vacuum-condensed on muscovite assumed the single- and triple-directional orientations.4) It turned out in previous investgations that the b-axes of crystals always ran parallel to the substrate surface.

When substrate muscovite was treated at a higher temperature in advance of the deposition of these materials, films of many phthalocyanine compounds showed quite a different orientation. Using these oriented films, the crystal data were determined for the metastable forms of several phthalocyanine derivatives by the high-resolution electron-diffraction method.5)

In this work, the effect of the thermal treatment of muscovite will be studied concerning the orientation overgrowth of copper-phthalocyanine. The orientation of the evaporated film of phthalocyanine will also be examined in relation to the substrate by electron microscopy as well as by electron diffraction.

Experimental

The metal-phthalocyanines used in this work was purified by repeated sublimation in a stream of carbon dioxide at low pressure and at a temperature above 500°C. A freshly-cleaved thin film of muscovite about 20 mm. square was placed in a Pyrex glass tube situated in an electric furnace. The substrate was heated at an appropriate temperature in a vacuum of about 5×10^{-5} mmHg. The purified material was then vacuum-sublimated onto muscovite following the

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1) J. Willems, *Z. Elektochem.*, **56**, 345 (1952).

2) W. Kleber and K. Meyer, *Z. anorg. u. allgem. Chem.*, **296**, 164 (1958).

3) E. Suito, N. Uyeda and M. Ashida, *Nature*, **194**, 273 (1962).

4) N. Uyeda, M. Ashida and E. Suito, *J. Appl. Phys.*, **36**, 1453 (1965).

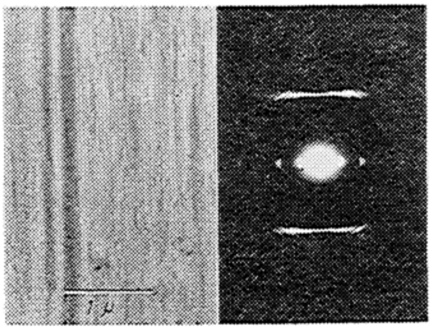
5) M. Ashida, N. Uyeda and E. Suito, This Bulletin, **39**, 2616 (1966).

same procedure as that described in the previous work.[5] The crystallographic principal axes of muscovite were determined in its basal plane by polarizing microscopy. The specimen used for electron microscopy was prepared by the wet-stripping method.

Results

Three Types of Orientation.—Films vacuum-condensed onto muscovite showed various orientations according to the evaporating conditions. Generally speaking, the typical orientations may be classified into the following three groups.

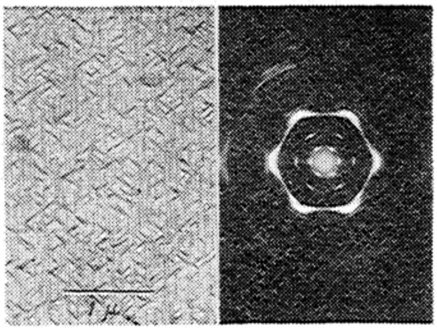
A. Parallel b-Axis Orientations. — *A-1. The Single-directional Orientation.*—When substrate muscovite was preheated at 300°C for one hour and then kept at a temperature between 150°C and 170°C, the film condensed showed a well-defined single-directional orientation, whose electron micrograph and electron diffraction pattern are shown in Figs. 1(a) and (b) respectively. As has been described in a previous paper,[4] films were composed of laminar crystal strips; it was revealed by the analysis of the fiber diagram obtained from the film that at least two kinds of lattice orientations may be assumed to show a longitudinal direction in individual strips which always run parallel to their b-axes. As for the relative orientation of the evaporated film to the substrate, the b-axis of the former was parallel to either of the two directions, which made $\pm 60°$ with the b-axis of the muscovite crystal.[6]



(a) (b)

Fig. 1. Electron micrograph (a) and electron diffraction pattern (b) of copper-phthalocyanine film which assumed the single-directional orientation.

A-2. The Triple-directional Orientation. — The triple-directional orientation was observed when films were prepared at the substrate temperature of 200°C without any preliminary thermal treatment. The electron micrograph shown in Fig. 2(a) exhibits that the film was built up of triangular labyrinthine networks of slender crystal strips.



(a) (b)

Fig. 2. Electron micrograph (a) and electron diffraction pattern (b) of copper-phthalocyanine film which assumed the triple-directional orientation.

Corresponding to such a configuration of the film, the diffraction pattern also had a hexagonal appearance, as Fig. 2(b) shows. The pattern is a superposition of three identical fiber diagrams, each of which is essentially the same as that of the single-directional orientation.

B. The Standing b-Axis Orientation.—When the substrate muscovite was heated in advance at 400°C for one hour and then kept at 150°C, the film was composed of small, flaky crystals which grew by orienting themselves along either of the two different directions designated as AA′ and BB′ in Fig. 3(a). These wedge-like crystals were separated from one another, making the total film discrete, unlike the above two cases. The electron diffraction pattern in Fig. 3(b) is apparently

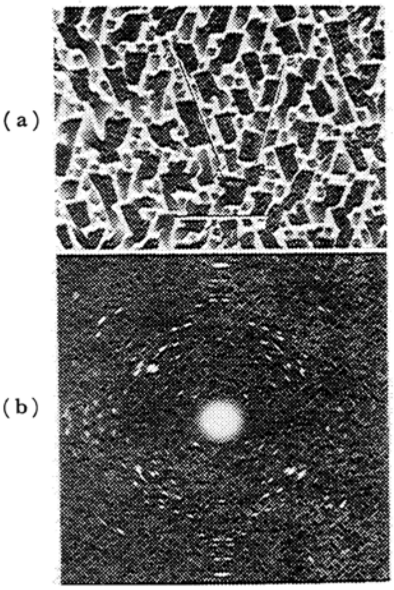


Fig. 3. Electron micrograph (a) and electron diffraction pattern (b) of copper-phthalocyanine film which assumed the standing b-axis orientation.

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6) E. Suito, N. Uyeda, M. Ashida and K. Yamamoto, *Proc. Japan Acad.*, **42**, 54 (1966).

a superposition of two identical diagrams, both composed of layered zones of reflection spots. Naturally, the angle defined by those two sets of parallel layered lines is identical with that defined by the two directions AA′ and BB′. The appearance of these layered zones in the individual diagrams should be ascribed to the position of the main zone axes of the evaporated crystal, which are tilted against the substrate face and, consequently, against the electron beam. This orientaion will be described in a later section.

The Relation between the Evaporating Conditions and the Orientation Overgrowth of Copper-phthalocyanine.—As has been described above, three groups of orientations of copper-phthalocyanine vacuum-condensed on muscovite take parallel b-axis orientations, which includes single- and triple-directional orientations, and the standing b-axis orientation. The appearance of these different orientations depends on the evaporating conditions, one of which is expected to be the thermal treatment of muscovite. In an effort to determine the effect of thermal treatment, the change in the orientation was also studied with various combinations of the time and the temperature of preheating; the effect of the temperature at which the material was finally deposited was also studied.

Generally, the film formed on substrate muscovite at room temperature was composed of granular crystals with a random orientation. An epitaxial growth of phthalocyanine occurred when the temperature of substrate was not lower than about 100°C. As the substrate temperature was increased, the deposited crystal grew larger and assumed a better orientation until around 200°C, above which point the orientation became worse again. When the substrate was kept at temperatures above 200°C, a film was built up of long, flaky crystals, which occurred in the stable form and which grew in a random direction, without any relative orientation to the substrate structure.

The effect of the preliminary thermal treatment of muscovite on orientation overgrowth is summarized in Fig. 4. In this case, the substrate temperature was kept at 150°C during sublimation for all the experiments. Since the single- and triple-directional orientations both take the b-axis of crystals parallel to the muscovite surface and occasionally mix with one another, the temperature range for the appearance of these orientations can not be defined by sharp critical points. When the temperature of the thermal treatment was under 350°C, the deposited crystals always assumed the parallel b-axis orientation, in which the single-directional orientation occurred only in a considerably limited range of temperature, as follows: the substrate muscovite was treated in advance at 300°C for one hour, and the substrate temperature during sublimation was kept in the range from 150°C to 170°C. The triple-directional orientation appeared under all conditions, except for the range of temperature mentioned above. On the other hand, when the thermal treatment was carried out above 350°C, the deposited crystals assumed the standing b-axis orientation. Therefore, the orientation overgrowth on muscovite was found to change its state from one to the other when the temperature of the preliminary thermal treatment was around 350°C. Moreover, when the substrate muscovite was exposed to water vapor after a thermal treatment at 400°C and then treated under 300°C in vacuo, the film condensed on it again showed a triple-directional orientation. Consequently, the alternation of orientation seems to depend on the variation in the surface structure of muscovite, which is not necessarily accompanied by the decomposition of the crystal lattice of the substrate but which occurs reversibly in regard to the temperature range mentioned above.

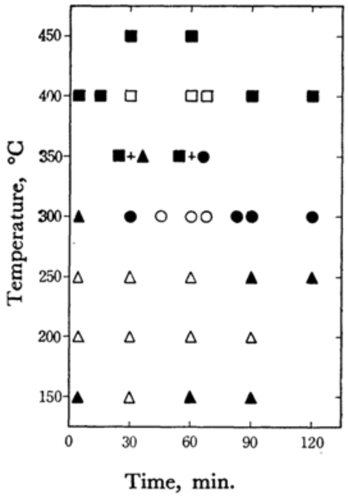

Fig. 4. The effect of preliminarily thermal treatment of muscovite on orientation overgrowth of Cu-phthalocyanine. The substrate temperature is kept at 150°C during sublimation.

□: Standing b-axis orientation
■: Nearly standing b-axis orientation
○: Single-directional orientation
●: Nearly single-directional orientation
△: Triple-directional orientation
▲: Nearly triple-directional orientation

The Determination of the Standing b-Axis Orientation.—Each elementary cross-grating pattern in Fig. 3(b) consists of three parallel zones. On the basis of the unit-cell constants of the metastable form,5) the reflection spots were indexed as in Fig. 5. The zone which includes the point of origin appears as the intersection of the reciprocal lattice points as well as their elongated intensity regions, which have the index of $k=0$ with the Ewald sphere. The other zones, which do not

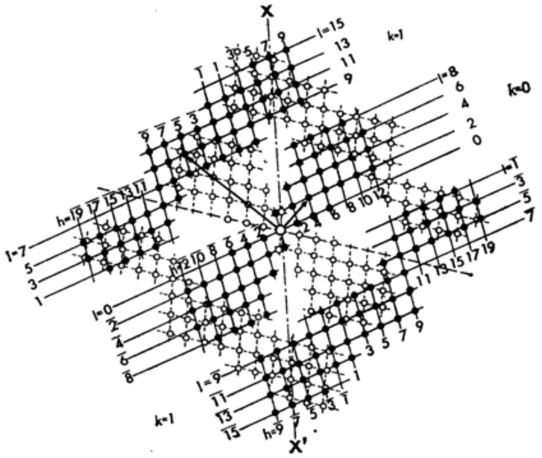

Fig. 5. The interpretation of the diffraction pattern shown in Fig. 3(b). A cross-section of the reciprocal lattice points of the crystal with the Ewald sphere. The reciprocal lattice points 402 and $\bar{5}19$ lie directly on the Ewald sphere.

include the point of origin, correspond to the reciprocal lattice planes of $k=\pm 1$. When the interplanar spacings obtained from the diffraction spots were compared with those calculated from the cell constants, the reciprocal lattice points, 402 and $\bar{5}19$, were found to lie directly on the Ewald sphere. Consequently, the a-, b- and c-axes of the crystal are inclined to the normal of the substrate surface at angles of about 75°, 32° and 118° respectively. On the other hand, the normal of the $(31\bar{3})$ plane is inclined to the a-, b- and c-axes at angles of about 69°, 33° and 113° respectively. When two sets of angles were compared, the crystal which assumed the standing b-axis orientation has its $(31\bar{3})$ plane almost parallel to the substrate face. The reflection diagram in Fig. 5 implies the plane of C_{2v} symmetry, XX', which was found to make an angle of 60° with the

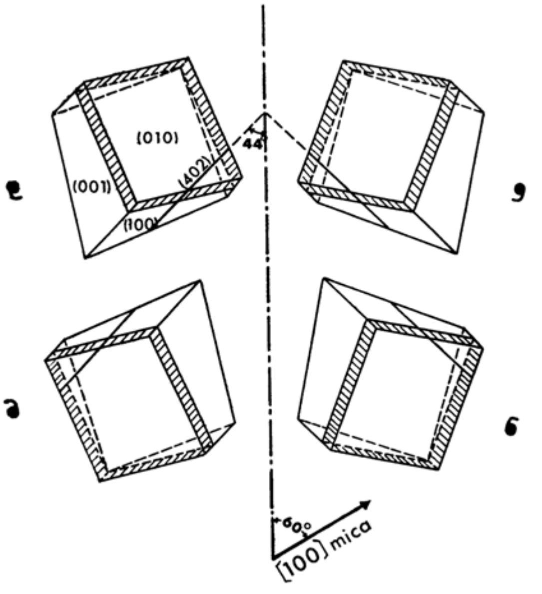

Fig. 6. Schematic diagram of the projection of crystals which assumed the standing b-axis orientation on the muscovite surface. The hatched zone shows unit cell dimensions. The (402) plane is perpendicular to the muscovite surface.

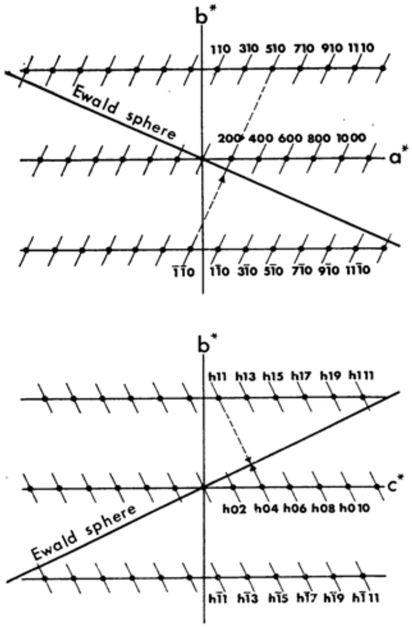

Fig. 7. Schematic diagrams of the elongation in the intensity region of the reciprocal lattice points. A: cross-section with 001 layer, B: cross-section with 100 layer.

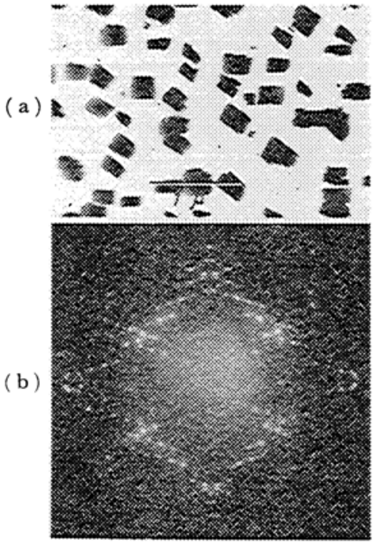

Fig. 8. Electron micrograph (a) and electron diffraction pattern (b) of platinum-phthalocyanine film which assumed the standing b-axis orientation.

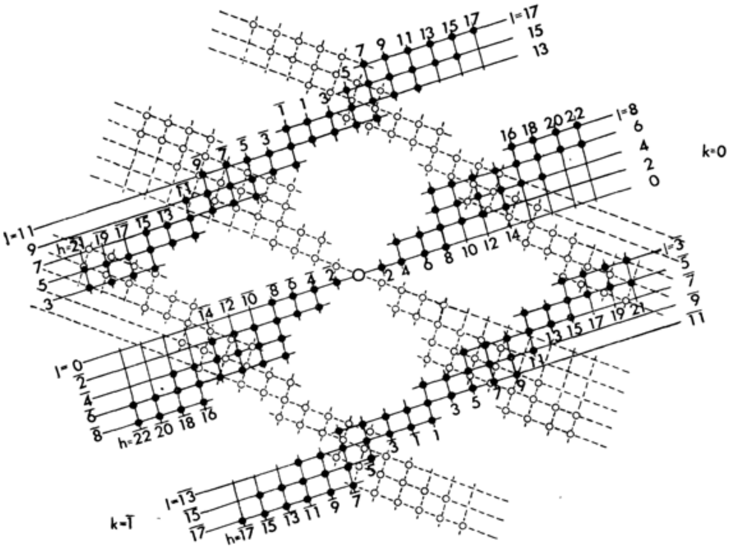

Fig. 9. The interpretation of the diffraction pattern shown in Fig. 8(b).

a-axis of muscovite. The projection of the crystals onto the muscovite face is shown schematically in Fig. 6, where the individual unit cells are designated with hatched zones. The orientation of these four crystals can be defined by two kinds of symmetries, one of which is a plane of mirror symmetry which makes an angle of 60° with the a-axis of muscovite and stands perpendicular to its surface, while the other is an axis of the two-fold symmetry. The projection of the b-axis of the evaporated crystals to the surface makes an angle of about 44° with the plane of symmetry. The top face of the crystal corresponds to the (010) plane, and the side faces, to the (100) and (001) planes.

In the diffraction pattern, the reflections which have the same value of *h* or *l* but which differ in the index *k*, did not appear on the same line. This was probably caused by the elongation in the intensity region in a somewhat unusual direction. Since the external form of the crystal is wedge-shaped, the thickness of the crystal measured normal to the (31$\bar{3}$) plane, which is almost parallel to the substrate face, may be very thin in the vicinity of the edge. Consequently, it may be supposed that the intensity regions of the reciprocal lattice points are elongated along the normal to the (31$\bar{3}$) plane and are crossed by the Ewald sphere, which is parallel to the basal plane of the crystal, as Fig. 7 shows. According to the figure, it is clear that the points with the indices of 51*l* fall on the same line as those with the indices of $\bar{1}\bar{1}l$; it is clear also that the line includes the points with the indices of 20*l*. Similarly, the points with the *h*1l indices fall on the same line as those with the *h*04 indices.

The standing b-axis orientation was also observed in other phthalocyanine compounds. Platinum-phthalocyanine, for example, assumed a similar orientation, as Figs. 8(a) and (b) show. The cross-grating pattern is interpreted as is shown in Fig. 9 by the method described above. In the case of platinum-phthalocyanine, it turned out that two reciprocal lattice points, 402 and $\bar{3}$19, lie directly on the Ewald sphere, and that the a-, b- and c-axes of the crystal which assumed the standing b-axis orientation made angles of about 74°, 35° and 120° respectively with the normal of the substrate face. The projection of the b-axis of the crystal onto the substrate face made an angle of about 44° with the plane of symmetry.

Discussion

Vacuum-condensed films of copper-phthalocyanine occur in the metastable form of its dimorphs and were found to be isomorphic with platinum-phthalocyanine.4) Such isomorphic behavior of the phthalocyanine derivatives has also been found in the case of stable crystals of beryllium-, iron- cobalt-, nickel-, copper- and metal-free phthalocyanines.7,8)

According to Robertson,7) the molecular plane has the same inclination of 45.8° to the b-axis in the cases of nickel- and metal-free phthalocyanines of the stable form. Therefore, the molecule in the metastable form of copper-phthalocyanine is expected to be inclined to the b-axis at an angle similar to that of the platinum derivative, which has a conspicuous isomorphic structure, although

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7) J. M. Robertson, *J. Chem. Soc.*, **1935**, 615.
8) R. P. Linstead and J. M. Robertson, ibid., **1935**, 1736.

no exact information has been obtained as far as copper-phthalocyanine is concerned. However, the relative orientation of platinum-phthalocyanine to the substrate may reasonably be interpreted on the basis of this isomorphism.

The crystal structure of the platinum derivative has the following unit cell dimensions with the monoclinic space group $C2/c$: $a=26.18$ Å, $b=3.818$ Å, $c=23.84$ Å, and $\beta=91.9°$.5) The molecules of platinum-phthalocyanine appear to be strictly planar and stack themselves so that they are closely packed in a column, facing each other, parallel, and inclined alternatively along the c-axis. The central platinum atom lies at the center of a square-bonded configuration with four nitrogen atoms, and four other nitrogen atoms make a bridge between the isoindole rings. The molecular axes, L and M, are defined through the center of the molecule and the latter nitrogen atoms (see Fig. 11). When a projection is taken normal to the molecular plane, the corresponding atoms in parallel molecules along the b-axis shift along the molecular axis, M, one from another. The angles between the molecular axes and the crystal axes are given in Table I. The normal direction of the $(21\bar{4})$ plane, which is approximately parallel to the substrate face, makes such angles with the crystal axes as are given in the last column of Table I. Because the discrepancy between the angles in the third column (N) and those in the last one was quite small, it is evident that the molecular plane is parallel to the surface of muscovite in this case. On the other hand, each molecule in the crystal with the parallel b-axis orientation stands on a carbon atom in one of the outer benzene rings.4) Consequently, when the crystal assumes the parallel or the standing b-axis orientation, the planar molecules in the individual crystals are located on the substrate face, as is shown schematically in Fig. 10. On the basis of this experimental finding, there may considered to be an atomic matching between the deposited and the substrate crystals at the interface.

TABLE I. ORIENTATION OF PLATINUM-PHTHALOCYANINE MOLECULE IN THE CRYSTAL

	Angles between molecular axes and crystal axes			Angles between crystal axes and the normal to the $(21\bar{4})$ plane
	L.	M.	N.*	
b-Axis	85.7°	63.9°	26.5°	31.0°
c-Axis**	71.4	32.9	116.1	123.0

* Molecular axis N is the normal to the molecular plane.

** The c-axis is transformed from the a-axis assigned by Robertson.

When it is tentatively assumed that the hexagonal network of potassium ions on the cleavage face is perfect and that a nitrogen atom on the molecular axis M (e. g., m), defined as the point of origin, is located on a potassium ion (e. g., K_1), one nitrogen atom on the molecular axis (e. g., p) is in contact with a potassium ion (e. g., K_2), and a nitrogen atom bonded to the central platinum atom (e. g., a) also comes into contact with a potassium ion (e. g., K_3) as is shown schematically in Fig. 11. The projections of the a-, b- and c-axes of the crystal onto the molecular plane are exhibited with a_p, b_p and c_p directively. In this case, the neighboring molecules are distributed on the substrate face as is shown in the figure. The closest molecule along the a-axis is located at the nearest site of potassium ions (e. g., K_4, K_5, K_6 and K_7) with four nitrogen atoms on the molecular axes (e. g., m′, n′, p′ and q′). Similarly, the next parallel molecule in the direction of the c-axis is located at the nearest site of potassium ions (e. g., K_8, K_9 and K_{10}) with three nitrogen atoms (e. g., n″, q″ and c″). If molecules are located on the surface of muscovite in such a manner, the direction of b_p, which is the projection of the b-axis of the crystal onto the substrate face, makes an angle of about 44° with the direction, K, which makes an angle of 60° with the a-axis of muscovite (a_M). The angle of 44° coincides with that between the plane of symmetry of the two different crystal orientations and the projection of the b-axis on the substrate face, which was formerly determined from the electron diffraction pattern. By a comparison of these two results, it may be confirmed that the orientation of the M axis and, consequently, all the molecules have an orientation such as is shown in Fig. 11. Because the phthalocyanine crystal has a symmetry of two-fold screw rotation and the molecule along the b-axis shifts in with the direction of $+$M or $-$M, the orientation of the deposited crystals has a symmtery of C_{2v}.

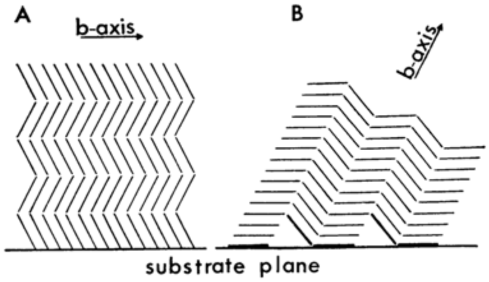

Fig. 10. Schematic diagrams of orientation of platinum-phthalocyanine molecules in the crystal. A: the crystal with the parallel b-axis orientation, B: the crystal with the standing b-axis orientation.

Although the top layer of muscovite apparently has a hexagonal symmetry, the orientation overgrowth of phthalocyanine compounds appeared only in a mirror symmetry. The plane of symmetry made ±60° with the a-axis of muscovite. As has been described in a previous paper,4) the

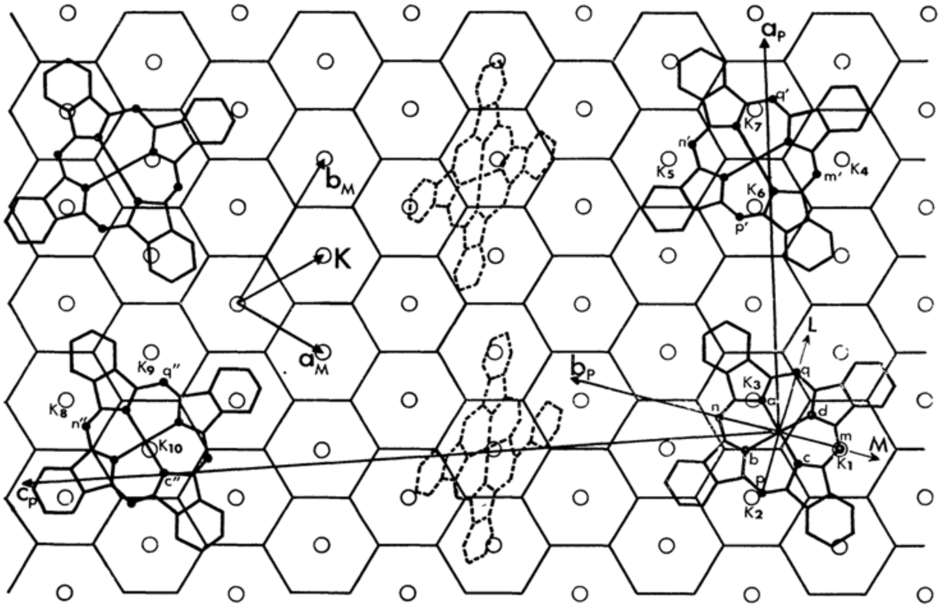

Fig. 11. Schematic diagram of the relative orientation of platinum-phthalocyanine to muscovite face when the crystal assumes the standing b-axis orientation. The directions a_M and b_M are the (100) and (010) directions of muscovite, respectively. Phthalocyanine molecules shown with dotted line are not contacted to the muscovite surface.

intersection of the plane of symmetry with the muscovite face coincides with the direction of the staggering in the top mica layer at the surface. It should be noted that the muscovite structure with a monoclinic symmetry, instead of a hexagonal one, gives rise to a latent influence upon nucleation and to a further growth of deposited films of phthalocyanine compounds, not only in the case of the parallel b-axis orientation, but also in the case of the standing b-axis orientation.

The orientation of the deposited crystal films varied from the parallel b-axis to the standing b-axis as a function of the thermal treatment of muscovite; there was quite a sharp critical transition point. The dehydroxylation of muscovite gradually begins at a temperature about 400°C in vacuo without a general destruction of the crystal lattice.[9] It is known that the phthalocyanine molecule, which has many aromatic rings, shows a strong repulsive force against water. Therefore, it is reasonable to postulate that the deposited molecules of phthalocyanine stand on the substrate muscovite so that the molecular planes separate from its surface as much as possible as a result of the repulsive force between the molecule and water included in muscovite. The resulting film shows a parallel b-axis orientation, whereas when the substrate muscovite was treated at 400°C, the planar molecule lies parallel to the substrate face because of the diminution of the repulsive force by the dehydroxylation of muscovite. The crystals thus nucleated by deposited molecules grow in the direction of the b-axis, which inclines obliquely to the substrate face, and the resulting film becomes discrete in the case of the standing b-axis orientation.

In the case of the metastable crystal of the copper-phthalocyanine film, which assumed the standing b-axis orientation, each crystal axis was observed to incline to the substrate face at an angle similar to that of platinum-phthalocyanine. Therefore, it seems that the molecular plane of copper-phthalocyanine inclines to the crystal axes at approximately the same angles as those of platinum-phthalocyanine. Consequently, it can reasonably be explained that the planar molecule of copper-phthalocyanine comes into parallel contact with the substrate face in a manner similar to that of the platinum derivative.

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[9] M. Ashida, T. Watanabe and W. Jono, This Bulletin, **39**, 2047 (1966).