BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2632—2638 (1966)

The Orientation Overgrowth of Metal-phthalocyanines on the Surface of Single Crystals. II. Vacuum-condensed Films of Copper-phthalocyanine on Alkali Halides

By Michio Ashida*

Institute for Chemical Research, Kyoto University, Takatsuki, Osaka

(Received May 2, 1966)

Cleaved faces of KCl, KBr and NaCl crystals were used as substrates. When copper-phthalocyanine is vacuum-condensed onto either KCl or KBr, the films on it take a standing b-axis orientation, which shows a C_{4v} symmetry. The major planes of symmetry coincide with those of KCl and KBr. The crystals on KBr show an azimuthal angular shift of about +12° or −12° in respect to the major symmetry axes, [010] and [100], of the substrate crystal. When the films have the standing b-axis orientation, the planar molecule in the crystal comes into parallel contact with the cleavage face of the substrate. It may be presumed that the bridge nitrogen atoms in a phthalocyanine molecule are placed on the potassium ions in the (001) planes of KCl and KBr. The films on KCl and KBr are composed of finely-divided rectangular crystals and dendrites; the former are concentrated at steps on the cleavage face to produce a decorative pattern, while the latter appear on the smooth surface. The formation in various types of crystals are interpreted in terms of the rate of nucleation and growth. The films vacuum-condensed onto NaCl are composed of laminar crystals which have a random orientation.

In previous papers,[1,2] the orientation overgrowth of phthalocyanine compounds was investigated on a cleavage face of muscovite. Films vacuum-condensed onto muscovite occurred in two different types of orientations, which were called the parallel b-axis orientation and the standing b-axis orientation. This difference appeared mostly to depend upon the condition of the thermal treatment of muscovite. With regards to the orientation of the phthalocyanine crystal relative to substrate muscovite, it was suggested that planar molecules in the crystal came into contact with the cleavage face of muscovite, and that bridge nitrogen atoms in a phthalocyanine molecule were connected with the surface potassium ions in the (001) plane of muscovite when the film took the standing b-axis orientation.

In an effort to elucidate the effect of potassium ions in a substrate on the orientation overgrowth of phthalocyanine, the vacuum-condensed film was studied on the cleavage faces of alkali halides. Karasek and Decius[3] reported that vacuum-sublimated films of metal-free phthalocyanine on rock salt appeared in either of its dimorphs, depending upon the substrate temperature. By X-ray diffractometry, they also found that the crystals were of the metastable form if the substrate temperature was lower than 200°C. However, they did not refer to the orientation of the deposited films relative to the substrate.

For the present paper, vacuum-condensed films of copper-phthalocyanine on cleavage faces of alkali halides were observed by electron microscopy. The appearance of various crystals in their growth process was then interpreted on the basis of the topography of the substrate surface. The orientation of the film was determined by electron diffraction. The orientation of the deposited crystal relative to the substrate alkali halides will be discussed on the basis of the molecular arrangement in the crystal.

Experimental

Powdery commercial copper-phthalocyanine was purified by repeated sublimation in a low-pressure stream of carbon dioxide at a temperature above 500°C. The purified material was sublimated from a tungsten basket onto the cleavage faces of alkali halides in a vacuum evaporator. The single crystals of alkali halides used in this work were potassium chloride, potassium bromide and sodium chloride. The crystals were cleaved in air and immediately placed in a Pyrex glass tube, as has been mentioned in a previous paper.[2] The specimens used for electron microscopy were prepared by the wet-stripping method.

Results

The Morphology of the Vacuum-condensed Crystals.—*(a) Crystals on the Cleavage Face of Potassium Chloride.* — When copper-phthalocyanine

---

* Present address: Depertment of Industrial Chemistry, Faculty of Engineering, Kobe University, Nada-ku, Kobe.

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

[2] M. Ashida, This Bulletin, **39**, 2625 (1966).

[3] F. W. Karasek and J. C. Decius, *J. Am. Chem. Soc.*, **74**, 4716 (1952).

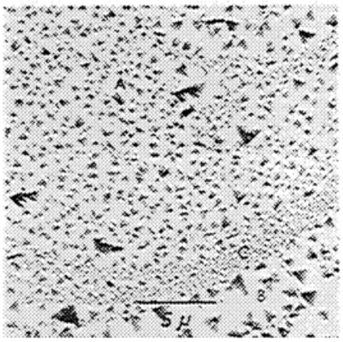
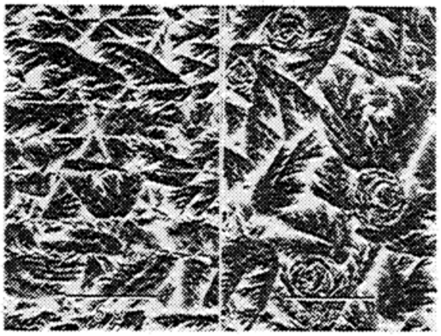


Fig. 1. Electron micrograph of Cu-phthalocyanine vacuum-condensed onto a cleavage face of KCl at the early stage of sublimation.



(a) (b)

Fig. 2. Electron micrographs of Cu-phthalocyanine films vacuum-condensed onto cleavage faces of KCl.

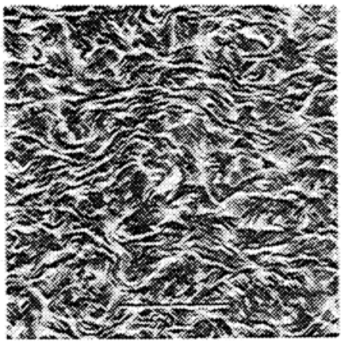
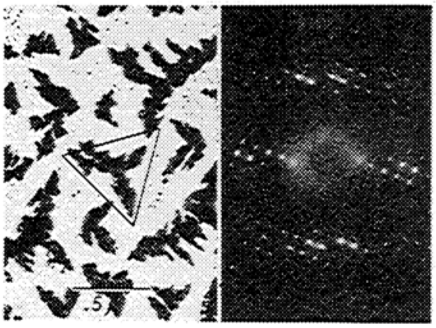


Fig. 3. Electron micrograph of Cu-phthalocyanine films vacuum-condensed onto a cleavage face of KCl when the rate of sublimation is increased.



(a) (b)

Fig. 4. Electron micrograph (a) and selected area diffraction pattern (b) of Cu-phthalocyanine vacuum-condensed onto a cleavage face of KCl at the substrate temperature of 200°C.

was vacuum-condensed onto a cleavage face of potassium chloride at 150°C, various crystal shapes were observed in the growth process of the deposit. At the early stage of condensation, the film was composed of three types of crystals, with different shapes, as is shown in Fig. 1. Very fine crystals like A, the size of which was about 100 Å, were observed all over the substrate face. In the part B, large dendrites appeared, while relatively small rectangular crystals came together in the part C. The curved pattern was formed by the latter crystals in the part B. As the film thickness was increased, the dendrites grew larger until the ends of their branches reached the curved zone, as is shown in Fig. 2(a), while small crystals condensed on the curved zone came into contact with each other without showing any tremendous growth. These curved lines formed by the crystallites may be attributed to the decorative effect similar to that pointed out by Basset and Pashley[4] for the metallic deposit on alkali halides and other inorganic crystals. It is well known that the decoration pattern shows the topography of the cleavage face. Sometimes, small crystals were observed to lie on concentric circles in the early stages. These crystals were aggregated in the circles to form a cabbage-like shape, shown in Fig. 2(b), when the amounts of the condensed crystals were increased. When the rate of deposition was increased, the film was composed of small crystals which were connected to form a wave-like pattern, as is shown in Fig. 3. When the substrate temperature was higher than 200°C, the film was composed of only discrete crystals with a dendrite structure, as Fig. 4(a) shows. Figure 4(b) shows a selected area-diffraction pattern from the triangular dendtrite shown in Fig. 4(a); this pattern revealed that the dendrite was a well-defined single crystal. Although the deposited crystal occurred in various types depending on either the condensation conditions or the topography of the cleavage face, all the crystals were found to have the same crystal habit on a close observation of electron micrographs as well as of electron-diffraction patterns. It is obvious that the dendrites shown in Figs. 1 and 4 are formed from rectangular crystals which were aggregated to one another with a definite orientation. The cabbage-like

---

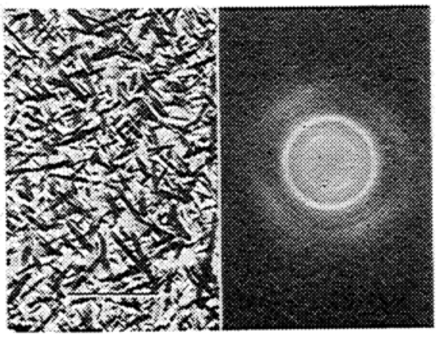
[4] G. A. Basset and D. W. Pashley, *Phil. Mag.*, **3**, 1042 (1958).

features in Fig. 2(b) are apparently composed of a number of small rectangular crystals assembled on the concentric circles. In the process of crystal growth, the difference in the way of the secondary aggregation of these elementary rectangular crystals gave rise to various shapes.

(b) Crystals on the Cleavage Face of Potassium Bromide.—When the cleavage face of potassium bromide was used as the substrate, the film vacuum-condensed on it was composed of small rectangular crystals and dendrites, as Fig. 5 shows, which were similar to those formed on potassium chloride. The small crystals arranged in a row were distributed all over the surface, as were the dendrites.

Fig. 5. Electron micrograph of Cu-phthalocyanine vacuum-condensed onto a cleavage face of KBr.

(c) Crystals on the Cleavage Face of Sodium Chloride.—In contrast to the film formed on either potassium chloride or potassium bromide, the film on sodium chloride was composed of crystals with entirely different features, as Fig. 6(a) shows. The laminar crystals grew in random directions, and the size of the crystals was apparently not uniform. No evident orientation was observed in the electron diffraction pattern, as may be seen in Fig. 6(b).



(a) (b)

Fig. 6. Electron micrograph (a) and diffraction pattern (b) of Cu-phthalocyanine vacuum-condensed onto a cleavage face of NaCl.

The Determination of the Crystal Orientation.—*(a) The Orientation of the Crystal Deposited on Potassium Chloride.*—Although the films condensed onto the cleavage face of potassium chloride were composed of crystals with various shapes, as has been described above, the electron diffraction patterns from those films, all gave the same pattern, as is shown in Fig. 7, this revealed that all the crystals assumed the same lattice orientation. The diffraction pattern consisted of four sets of identical cross-grating patterns, each of which was essentially the same as the single crystal pattern shown in Fig. 4(b). Therefore, it turned out that the film included eight groups of crystals, in each of which the orientation was the same. The total diffraction pattern is schematically reproduced in Fig. 8, in which the white circles represent the basic single crystal pattern associated with the two groups of the crystals which have a C_2 symmetry. Although the total pattern appeared to be complicated, it can be configurated

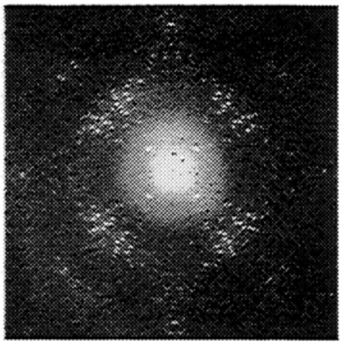


Fig. 7. High resolution electron diffraction pattern of Cu-phthalocyanine film vacuum-condensed onto a cleavage face of KCl. Crystals assume the standing b-axis orientation.

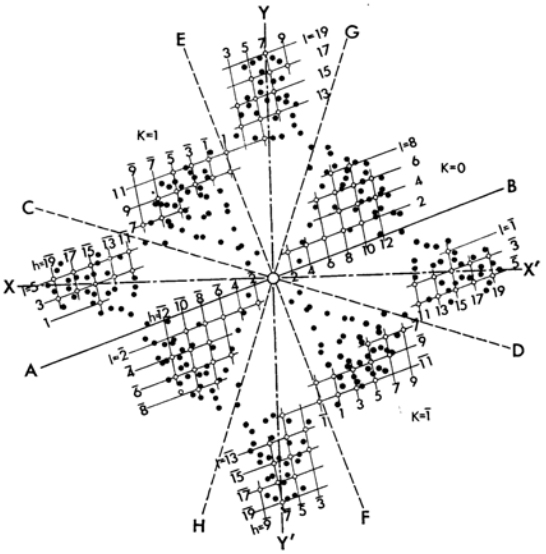


Fig. 8. The interpretation of the diffraction pattern shown in Fig. 7. White circles are the representation of the basic single crystal pattern.

by the systematic superposition of this elementary pattern, which is essentially the same as that shown in Fig. 4(b), with the major axes of C_{4v} symmetry, XX′ and YY′, which further coincide with the [100] and [010] directions of potassium chloride respectively.

Another result derived from the analysis of this elementary pattern is that the individual crystals have the $(31\bar{3})$ plane as the basal one facing parallel to the substrate crystal. As the AB line appears as the projection of the c* reciprocal axis in the elementary pattern, so other lines, CD, EF and GH, are similar projections of c* axes associated with individual crystal groups. The angle between the projection of each c* reciprocal axis and the nearest major axis of symmetry was found to be almost 20°.

(b) The Orientation of the Crystal Deposited on Potassium Bromide.—The films condensed onto potassium bromide were composed of crystals similar to those on potassium chloride, excepting that the high-resolution electron-diffraction pattern from the film revealed a somewhat different orientation of the deposited crystals. Figure 9 shows the electron-diffraction pattern obtained from the film. Also, in this case the crystals turned out to assume the standing b-axis orientation, in which the $(31\bar{3})$ plane of the crystal lies parallel to the cleavage face of potassium bromide. The pattern indicated that the orientation of crystals has a C_{4v} symmetry, the major axes of which again coincide with the [010] and [100] directions of potassium bromide. Therefore, the crystals may be classified into eight orientation groups, defined by two planes of symmetry which finally coincide with the (100) and (010) planes of potassium bromide; these planes are designated by XX′ and YY′. The arc spots revealed that crystallites included in the individual groups were oriented with an azimuthal angular shift of about 12°. Thus, the projection of the reciprocal c* axis on the basal plane falls into an angular range defined, for instance, by AB and A′B′ for one group of crystallites. Since the pattern has the C_{4v} symmetry, the angular ranges of the projection of the c* axis are defined by sets of CD:C′D′, EF:E′F′ and GH:G′H′ for the other groups, as is shown in Fig. 10. Even in this case, each crystallite condensed onto potassium bromide again occurred in the standing b-axis orientation, which made the $(31\bar{3})$ plane parallel to the substrate surface.

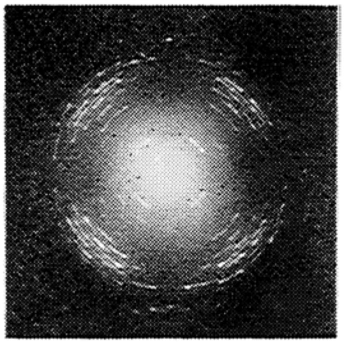


Fig. 9. High resolution electron diffraction pattern of Cu-phthalocyanine film vacuum-condensed onto a cleavage face of KBr.

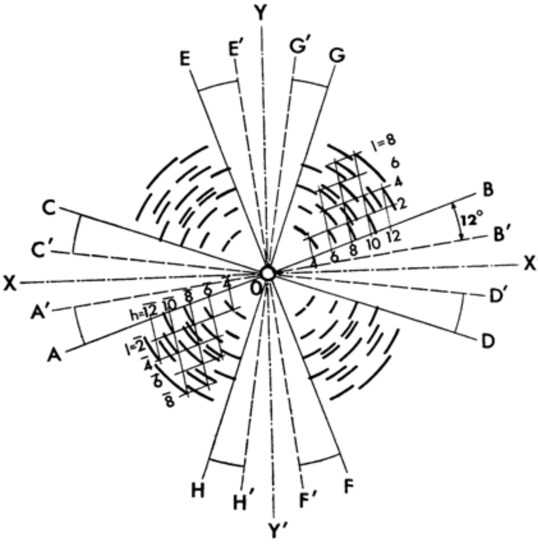


Fig. 10. The interpretation of the diffraction pattern shown in Fig. 9.

Discussion

As has been described in the previous paper,¹⁾ vacuum-condensed films of copper-phthalocyanine occur in the metastable form, the crystal structure of which is isomorphic with that of the platinum derivative. The a-, b- and c-axes of the copper-phthalocyanine crystal in the standing b-axis orientation are inclined to the normal of the substrate surface at angles of about 75°, 32° and 118° respectively. In the case of the platinum-phthalocyanine crystal with the standing b-axis orientation on muscovite, the main axes are inclined to the normal of the substrate face at angles similar to those of the copper derivative, and the molecular plane faces the substrate face.²⁾ Therefore, it seems that the molecular plane of copper-phthalocyanine in the alternative lattice rows in the basal face comes into parallel contact with the substrate face. The metastable form of copper-phthalocyanine has the following unit cell dimensions with a monoclinic space group $C2/c$: $a=25.82$ Å, $b=3.79$ Å, $c=23.72$ Å and $\beta=90.4°$.⁵⁾ As the

---

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

axial angle, β, is nearly equal to a right angle, the a* and c* axes of the reciprocal lattice are approximated by the directions along the a- and c-axes of the real crystal respectively. Consequently, the projection of the reciprocal c* axis on the basal plane shown in Figs. 8 and 10 may be considered the projection of the c-axis on the substrate face.

The cleavage face of the potassium chloride crystal is the (001) plane, in which K^+ ions and Cl^- ions are alternatively located in the [100] and [010] directions at the distance of 3.14 Å, as is shown in Fig. 11. A phthalocyanine molecule is usually represented by a set of two molecular axes, L and M, which are defined through the center of the molecule through the bridge nitrogen atoms, as Fig. 11 shows. A projection of the c-axis of the crystal on a molecular plane makes an angle of about 20° with the M molecular axis, and the b-axis of the crystal is projected on a molecular plane in the direction of the M molecular axis.

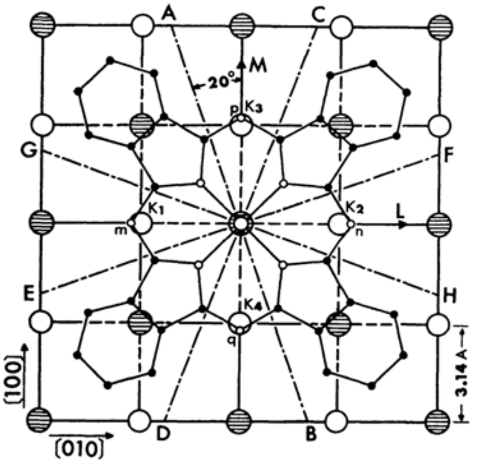


Fig. 11. The lattice structure of the cleavage face of KCl and the orientation relative to the deposited molecule of Cu-phthalocyanine.

According to Kobayashi,[6] the electrons in the phthalocyanine molecule are distributed on the bridge nitrogen atoms at the highest density; this causes an electrophilic effect to occur at these nitrogen atoms.[7] As the potassium ion has an electron-attractive force, the bridge nitrogen atoms of phthalocyanine possibly tend to come closer to the potassium ion. In the case of crystals deposited on potassium halides, it seems reasonable to consider that the bridge nitrogen atoms of the molecule which parallelly faces the (001) plane of the substrate crystal come into contact with the potassium ions on the cleavage plane. When it is tentatively assumed that four nitrogen atoms on the L and M molecular axes (e. g., m, n, p and q) are located on potassium ions (e. g., K_1, K_2, K_3 and K_4), the projection of the c-axis of the crystal on the substrate plane makes an angle of either +20° or −20° with the [100] direction of potassium chloride, as is shown by the line AB or CD; these lines give rise to two crystals with a plane of mirror symmetry, as is shown in Figs. 12 A and B. It should be noted that this angle coincides with that between the projection of the reciprocal c* axis of the phthalocyanine crystal and the [100] direction of potassium chloride as revealed by the electron-diffraction pattern. In addition to this choice of the c-axis, the above molecule parallel along the b-axis shifts in either the +M or −M direction depending upon the staggering of the overlapping molecule; this results in two different crystals by the axis of two-fold symmetry, as is shown in Figs. 12 A and C. The M molecular axis can also lie parallel to the [010] direction of potassium chloride; that is, the staggering of the overlapping molecule may happen in four other ways in the [010] direction, thus forming a final crystal which has a projection of the c-axis like either EF or GH. Thus, the total film configuration involves a C_{4v} symmetry as far as the orientation of the individual crystallites is concerned.

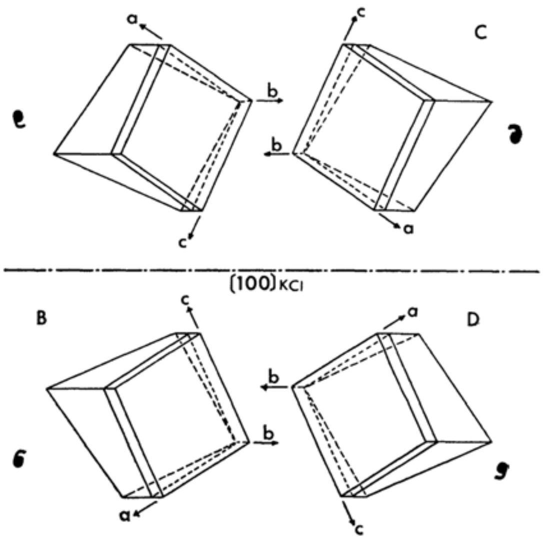


Fig. 12. Schematic diagram of the projection of crystals on the cleavage face of KCl.

Even though the same standing b-axis orientation appeared on potassium chloride, the crystal deposited onto potassium bromide showed an apparent azimuthal angular shift in the plane of the film. A cleavage face of potassium bromide is the (001) plane, in which K^+ ions and Br^- ions are located in the [100] and [010] directions at a

---

[6] H. Kobayashi, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **82**, 272 (1961).

[7] C. J. Pedersen, *J. Org. Chem.*, **22**, 127 (1957).

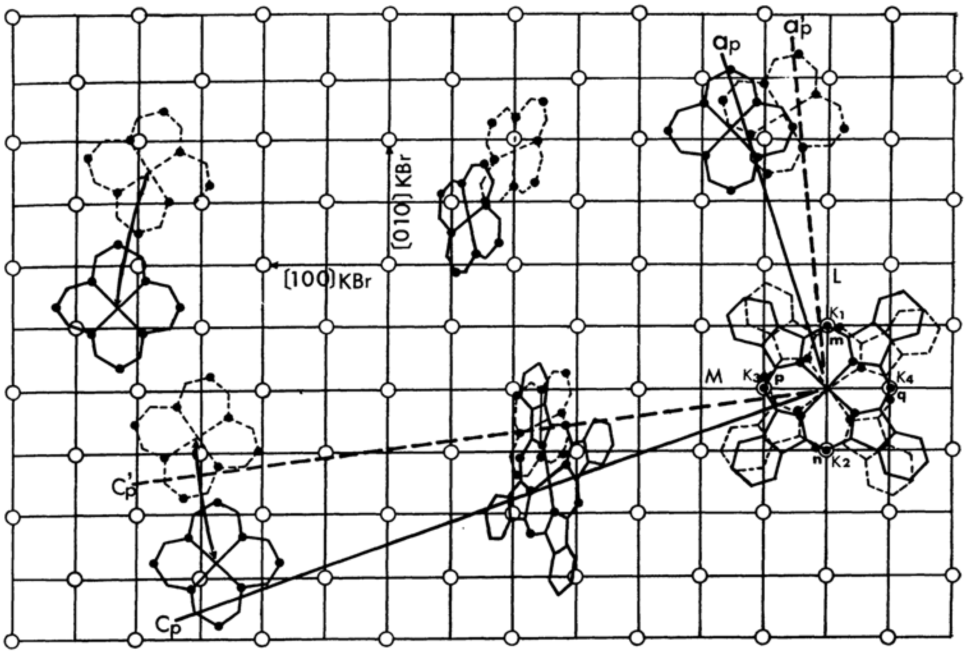


Fig. 13. The lattice structure of the cleavage face of KBr and the orientation relative to the deposited molecule of Cu-phthalocyanine.

distance of 3.29 Å, as is shown in Fig. 13. As has been described above, if four nitrogen atoms on the L and M molecular axes (e. g., m, n, p and q) of phthalocyanine, defined as the point of origin, are located on potassium ions (e. g., K_1, K_2, K_3 and K_4), the nitrogen atoms in the neighboring molecules are projected on the substrate face as is shown schematically in the figure. In this case, the projection of the c-axis, C_p, makes an angle of 20° with the [100] direction of potassium bromide. This angle coincides with that between the projection of the reciprocal c* axis of the phthalocyanine crystal, AB, and the [100] direction of potassium bromide as is revealed by the electron diffraction in Fig. 9. Since the orientation of the deposited crystals is distributed in an angular range of about 12° in azimuth, the projection of the c-axis lies between C_p and C_p'; that is, the molecules in the crystal may be rotated on the substrate face as is shown by the dotted line. The above characteristic orientation may plausibly be ascribed to the difference in misfitting between the deposit and the substrate crystal. The interaction betweeen the molecule and the substrate will also vary depending upon the differences in the negative ions.

The deposited crystals of phthalocyanine appeared in a C_{4v} symmetric orientation on the (001) planes of potassium chloride and potassium bromide. The planes of mirror symmetry corresponded to the (100) and (010) planes of potassium halides. On the contrary, phthalocyanine crystals deposited onto the (001) plane of muscovite, which apparently has a hexangonal symmetry, showed only a C_{2v} symmetry,1,2) this symmetry was considered to be due to the influence of the staggering in the mica layer under the cleavage face. This suggestion was supported by the present finding that the orientation of the phthalocyanine crystal had the same symmetry as that of the substrate face in the case of alkali halide, which has no such staggering as muscovite.

The crystal growth of evaporated films consists of two factors, the rates of nucleation and its growth. A variation in the crystal shape is caused by the contribution of the two factors. When phthalocyanine is deposited onto a cleavage face of potassium chloride, the preferential nucleation occurs at steps on the substrate face. Fast nucleation causes a number of fine crystals at the steps. On the contrary, the deposited molecule can relatively freely move over the smooth parts of the surface; thus it collides with other deposited molecules to form a large aggregate, and the nuclei grow to a large dendrite on these parts. As the rate of sublimation is increased, the deposited molecules have more chance to collide, thus leading to the nucleation predominate in number. Therefore, fine crystals appeared all over the surface with uniform dimensions and formed a continuous film with a wave-like pattern, as is shown in Fig. 4. In contrast to the crystals deposited onto potassium chloride, the film formed on muscovite was composed of small rectangular crystals; dendrites were not observed even when the film had the same standing b-axis orientation.²⁾ Since a cleavage face of muscovite is considered to be fairly smooth in an atomic scale over a limited area, this appearence is probably due to the difference in nucleation velocity. It seems that the molecules deposited onto muscovite have a lower mobility than those on potassium chloride, and that the difference in mobility depends upon the bonding force of the interface between deposit and the substrate.

Recently, Ino et al.⁸⁾ investigated the epitaxial growth of metal on a surface of sodium chloride which has been cleaved either in an ultrahigh vacuum of 10^{-7} to 10^{-9} mmHg or in a rather poor vacuum of 10^{-4} to 10^{-5} mmHg; they concluded that some gas molecule adsorbed on the sodium chloride surface is necessary for the epitaxial growth of a single crystal of f. c. c. metal. Furthermore, Mattews and Grünbaum⁹⁾ established that moist air modified the (001) plane of sodium chloride in such a way that f. c. c. metals tend to grow epitaxially upon it. In the present experimental results, the film condensed on sodium chloride has a random orientation. Phthalocyanine as well as condensed polycyclic aromatic compounds repulse water rather strongly. Since adsorbed water molecules could not be removed from the cleavage face of sodium chloride under the present experimental conditions, it is reasonable to postulate that the orientation overgrowth of copper-phthalocyanine on sodium chloride is disturbed by the adsorbed water molecules. This assumption was further confirmed by the use of sodium chloride cleaved in vacuo. In this case, the deposited crystals were found to have the standing b-axis orientation. The results will appear in detail in a future report.

The author is very grateful to Professor Eiji Suito of the Institute for Chemical Research, Kyoto University, for his interest and support; he wishes also to thank Dr. Natsu Uyeda of the same Institute for his many helpful discussions and suggestions during this work. Moreover, he is indebted to Professor Wasaburo Jono and Professor Teizo Watanabe of Kobe University for their encouragement in this work.

---

8) S. Ino, D. Watanabe and S. Ogawa, *J. Phys. Soc. Japan*, **19**, 881 (1964).

9) J. W. Matthews and E. Grünbaum, *Appl. Phys. Letters*, **5**, 106 (1964).