

# Some Behavior and Structures of Leaf-Like Crystals of Copper- and Zinc-Phthalocyanines Vacuum-Deposited by Electron Bombardment

Natsu UYEDA and Eiji SUITO\*

(Suito Laboratory, Institute for Chemical Research, Kyoto University)

*Received January 20, 1965*

When powderly crystals of Cu- and Zn-phthalocyanines were electron-bombarded in an electron microscope, thin networks of slender leaf-like crystals are formed on the supporting film. By selected area electron diffraction, it was revealed that the newly formed crystals were always the metastable  $\alpha$ -form regardless of the crystal form of the original powder in the case of Cu-phthalocyanine. As to Zn-phthalocyanine, similar leaf-like crystals take different forms depending on the locality of the substrate film. The stable  $\beta$ -form was found near the center of the hole of a grid mesh, whereas the metastable  $\alpha$ -form appeared on the film near the rim of the same hole. This variation was interpreted on the basis of the temperature distribution of the film caused by the electron irradiation. It is plausible that Zn-phthalocyanine has lower critical point (or so-called transition temperature) than Cu-derivative, at which two temperature ranges where the individual crystal forms are stable is separated. With a cross grating pattern obtained from a large leaf-like lamella of Cu-phthalocyanine, the metastable  $\alpha$ -form was interpreted to have a crystal structure different from that reported by Robinson and Klein.

## INTRODUCTION

Although it was briefly reported by German investigators<sup>1)</sup> that some of the metal phthalocyanine compounds had dimorphs, Hamm and van Norman<sup>2)</sup> were the first to report the dimorphic transformation of copper phthalocyanine as well as indanthrene blue on the basis of electron microscopy. In their investigation, the transformation observed under an electron microscope took place by the bombardment of electron beam. It was revealed that the original powderly specimen turned into thin networks of slender leaf-like crystals for both materials. Sasaki, Ueda and Kubota<sup>3)</sup> also observed a similar phenomenon in regard to powderly specimen of copper phthalocyanine.

In the course of electron microscopy and diffraction study of the transformation of copper- and zinc-phthalocyanines which were treated in some organic suspension media, we also found such phenomena of spontaneous transformation accompanied by the recrystallization of new forms with slender leaf-like strips. The results with copper derivative were compared with those obtained by Hamm and van Norman and some discrepancy was found as will be discussed hereunder. In the case of zinc phthalocyanine the variation of the crystal form was found, depending on the locality of the substrate film and was interpreted in terms of the temperature distribution of the film irradiated by the electron beam.

## EXPERIMENTS

It is a common sense in the ordinary electron microscopy to use a well-dispersed

---

\* 植田 夏, 水渡英二

specimen for the observation of powdery materials. However, rather poorly dispersed specimens with dense agglomerates of the powder material were preferred in this experiment where the bombardment of electron beam had the triggering effect for the unstable crystal to be recrystallized, since it has been well known that the thicker the specimen is, the more the energy of the hitting electrons can be accumulated in the materials. Copper phthalocyanine of both forms, the metastable  $\alpha$ -form and the stable  $\beta$ -form, were used as the specimens. The metastable form of zinc phthalocyanine was also chosen for the matter of comparison of the recrystallization effect. The metastable form of both compounds were prepared by the acid-paste method which has been widely applied in the industrial procedure for the purification as well as for obtaining the fine powder of these coloring materials. It is well known<sup>4)</sup> that some metal phthalocyanines of the metastable form, particularly those that obtained by the acid-paste method, also undergo the spontaneous transformation and crystal growth to the stable one when treated in organic suspension media. Thus, the copper phthalocyanine of the stable form used in this investigation was obtained by boiling the metastable form in pyridine for more than an hour. The resulting crystals appeared as slender needle-like strips of some 5 to 10 microns in length while the original material of the metastable form assumed rather flaky outlook for both compounds.

A small amount of each powder with a lot of agglomerates in it was mounted on a specimen grid for the electron microscopy, which was covered with a thin Formvar film. As it turned out, the variation in the supporting film also showed some influence on the outlook of the recrystallized specimen. And the Formvar film gave rise to the most systematic result among many other different films including collodion, carbon and so forth.

Observation was carried out under an electron microscope first with reduced electron beam current. After the selection was set with a suitable agglomerate, the beam current was increased so that the ordinary brightness of the image was attained. The evaporation from the agglomerate took place as its size gradually became smaller and simultaneously the networks of slender leaf-like strips of the newly formed crystals appeared on the empty area of the supporting film around the original agglomerate. In this case, the networks of thin crystals gradually increased the contrast all over the total area at the same time just as if latent images were developed by a photographic process. Selected area electron diffraction patterns were also obtained with various parts of these networks as well as crystalline islands in addition to the electron micrographs of the same areas.

## RESULTS AND DISCUSSION

The examples of the networks of recrystallized leaf-like thin lamellae are shown in Fig. 1 for both compounds. Apparently these two networks are very much alike to each other, although in the networks of Cu-phthalocyanine (a) small crystalline islands with random orientation are also observed in the left half of the photograph. The pericarp-shaped part in the top-left is composed of needle-like crystals that grew directly from a small agglomerate of the original powder.

Ordinarily, when these materials are vacuum deposited onto a substrate at room tem-

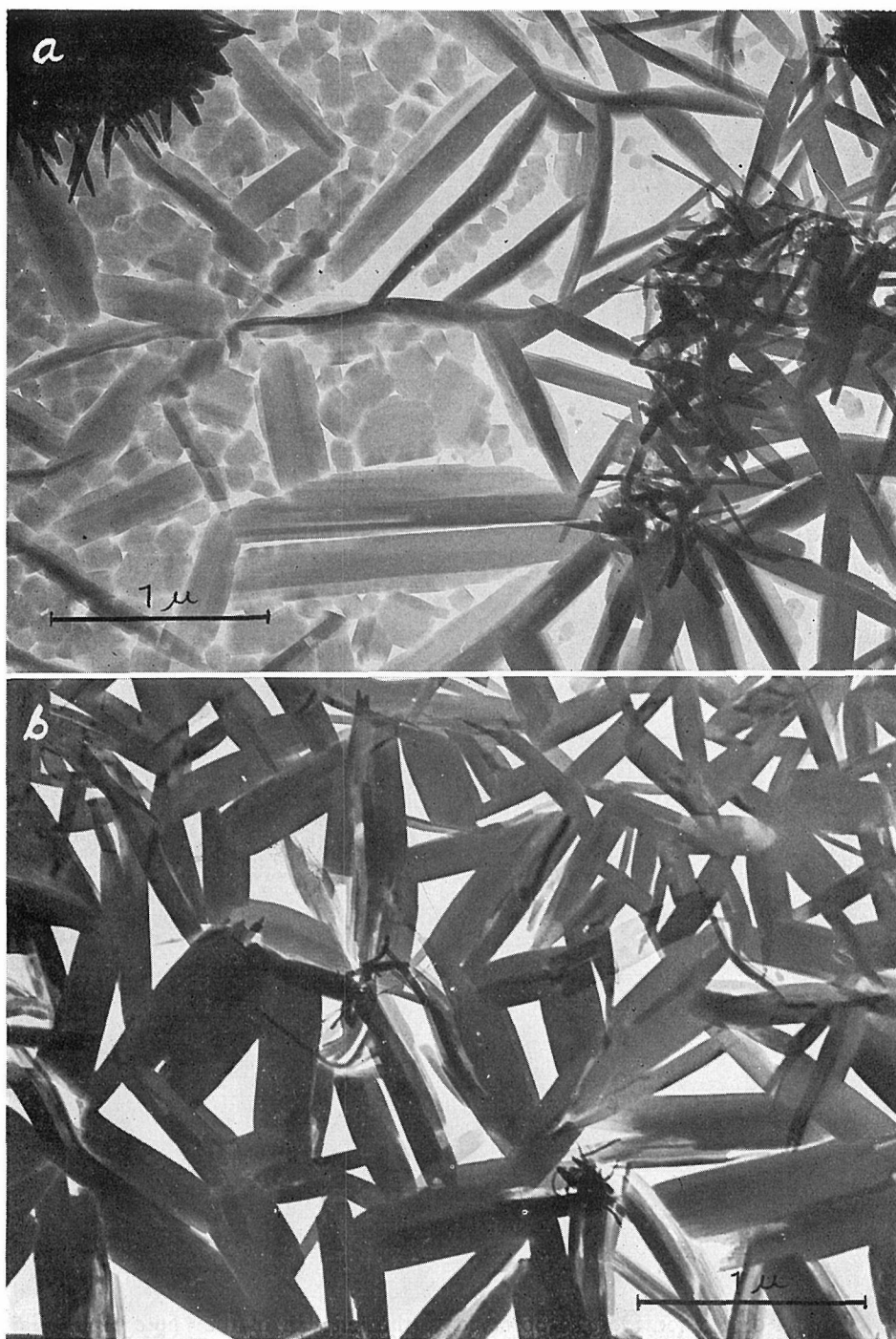


Fig. 1. Networks of leaf-like crystals of (a) Cu-phthalocyanine and (b) Zn-phthalocyanine that grew by electron bombardment.

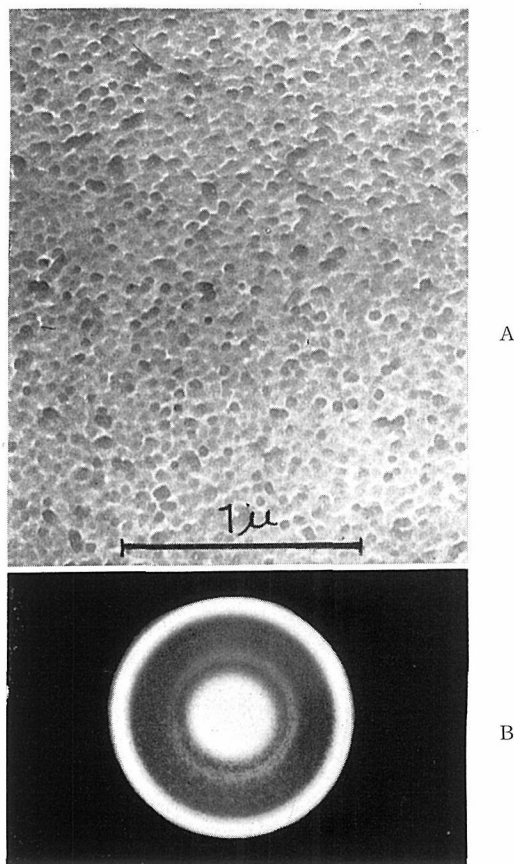


Fig. 2. Thin film of Cu-phthalocyanine artificially vacuum evaporated substrate film of Formvar at room temperature and the electron diffraction pattern.

perature, the resulting film gives rise to very fine particles of about  $10\text{ m}\mu$  in diameter as shown in Fig. 2, as an example for Cu-phthalocyanine. The electron diffraction pattern (B) shows that these fine particles take the metastable form. However, if the substrate temperature is as high as  $150^{\circ}\text{C}$  or more, the deposited crystals become slender laminar strips, very often showing some epitaxial orientation on the cleaved faces of some single crystals such as mica as reported in the previous paper<sup>5</sup>. Many phthalocyanine compounds often have a way of taking slender lathy crystal shape regardless of their crystal modifications. In these networks the angles with which these strips meet one another are rather irregular suggesting that the growth mechanism does not depend on the dendritic process. Fig. 3 is a similar network of evaporated thin film of copper compound. The bottom is closer to the center of the hole of the supporting grid mesh. It has been known that the temperature of the supporting film changes depending on the locality, and the center of a hole, of the grid mesh, caused by the bombardment of the electron beam and also by the poor thermal conductivity of the film, is always heated much heavier than the other part. Thus, it can be anticipated

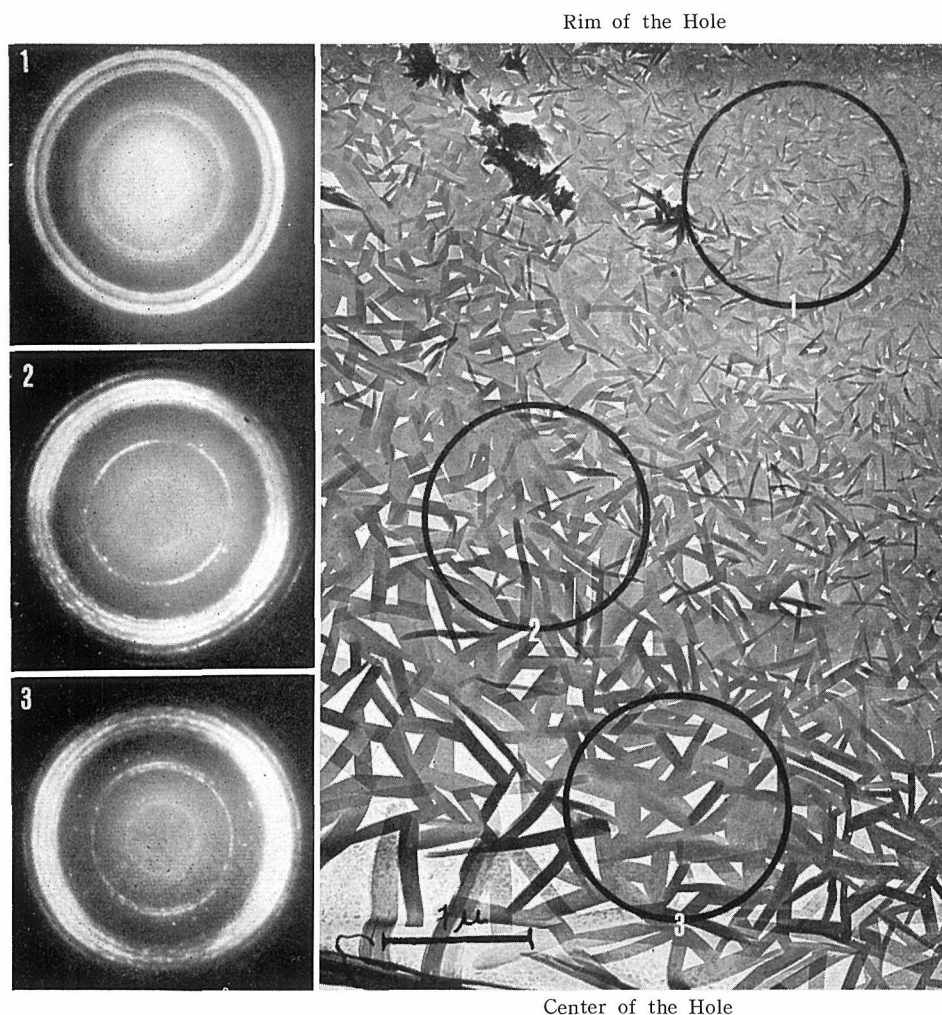


Fig. 3. Networks of Cu-phthalocyanine crystal leaf and selected area electron diffraction patterns.

that the difference in the crystal size is mainly due to the distance from the source as well as to the substrate temperature. The selected area electron diffraction patterns of the encircled parts designated by 1, 2 and 3 are reproduced respectively in the same order. Although the rings are rather spotty for the part 3 where rather large strips appeared, the crystals are identified to be the metastable  $\alpha$ -form. The diffraction pattern is essentially the same as the other ones in 2 and 3. This was confirmed by a comparison with the high resolution electron diffraction pattern obtained from the total area of the similar specimen as shown in Fig. 4. In this figure, the pattern A was taken at the normal incidence of electron beam to the specimen surface and the pattern B is the one obtained at a tilted position, which apparently shows the preferential orientation of the networks on the film. Table 1 shows the interplanar spacings calculated from these diffraction patterns, and the comparison with the data for ordinary metastable form shows that the networks

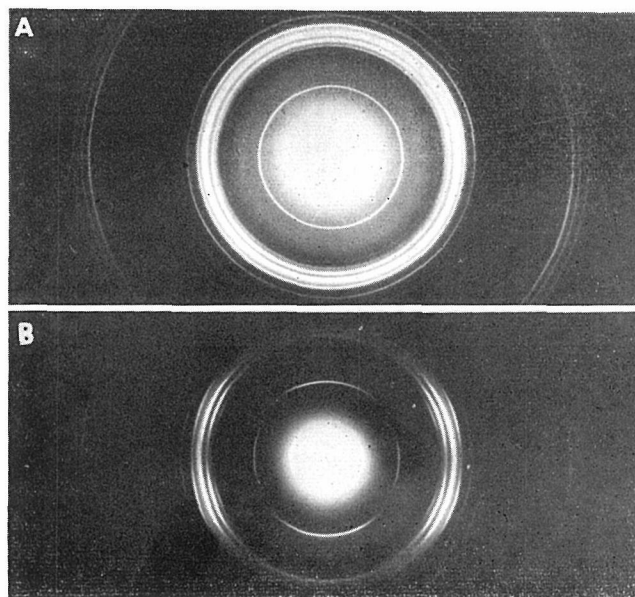


Fig. 4. High resolution electron diffraction of the leaf-like crystals of Cu-phthalocyanine at normal position (A) and tilted position (B) that shows the preferential orientation of the crystal leaves.

Table 1. Interplanar spacings of Cu-phthalocyanine evaporated by electron bombardment.

| $d_{\text{obs}}$ (Å) | $I/I_0$ | $hkl^*$ | $d_{\text{calc}}$ (Å) | $d_{\text{obs}}$ (Å)** |
|----------------------|---------|---------|-----------------------|------------------------|
| 11.86                | s.      | 200     | 11.892                | 11.90 s.               |
| 5.94                 | m.      | 400     | 5.946                 | 5.99 m.                |
| 3.96                 | w.      | 600     | 3.964                 | 4.01 m.                |
| 3.78                 | m.      | 010     | 3.785                 | 3.78 m.                |
| 3.72                 | m.      | 110     | 3.730                 | 3.72 s.                |
| 3.61                 | m.      | 210     | 3.607                 | 3.60 m.                |
| 3.42                 | v.s.    | 310     | 3.416                 | 3.33 m.                |
| 3.20                 | s.      | 410     | 3.193                 | 3.20 m.                |
| 2.96                 | m.      | 510     | 2.962                 | 2.97 m.                |
| 2.53                 | w.      | 710     | 2.528                 |                        |
| 2.35                 | w.      | 810     | 2.338                 |                        |
| 2.17                 | w.      | 910     | 2.167                 |                        |
| 1.893                | m.      | 120     | 1.887                 |                        |
| 1.853                | m.      | 320     | 1.851                 |                        |
| 1.809                | w.      | 420     | 1.804                 |                        |
| 1.765                | m.      | 520     | 1.759                 |                        |
| 1.711                | m.      | 620     | 1.708                 |                        |
| 1.625                | w.      | 720     | 1.654                 |                        |

\* The  $hkl$  given here was tentatively assigned for  $a=23.784\text{\AA}$  and  $b=3.785\text{\AA}$ .

\*\* These values are obtained from artificially vacuum evaporated thin films of the metastable Cu-phthalocyanine.

of the leaf-like crystal strip consist of the metastable  $\alpha$ -form. Thus, when Cu-phthalocyanine is incidentally vacuum deposited by electron bombardment, the structure of the newly formed crystal is essentially the same as the original one, the metastable  $\alpha$ -form, in contrary to the results reported by Hamm and van Norman.

Fig. 5. is another example of evaporated films of Cu-phthalocyanine, which was

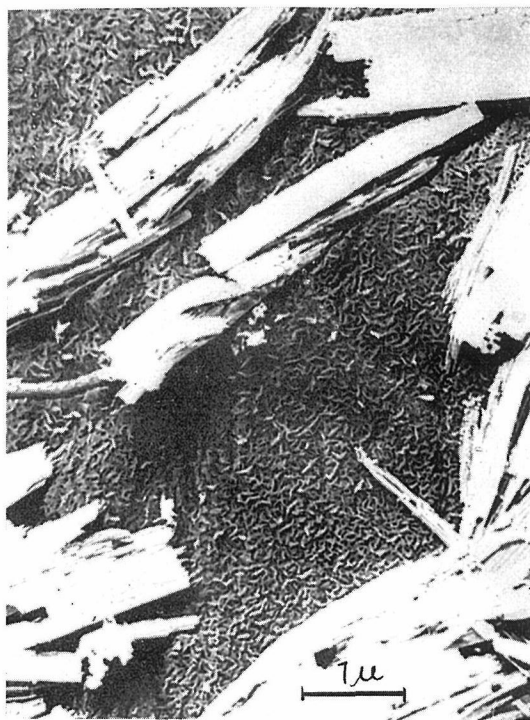


Fig. 5. Small metastable crystal flakes of Cu-phthalocyanine obtained by the evaporation of lathy stable crystals by electron bombardment.

obtained by the electron bombardment of the stable  $\beta$ -form crystals. In this case, the slender bundles of needle-like crystals are the original copper phthalocyanine of the stable form, which were prepared by boiling the metastable powder in pyridine and confirmed to be the stable one by X-ray diffractometry. The thin film of flaky small crystals that filled up the empty part is the one obtained by the bombardment of the electron beam. The selected area electron diffraction pattern also showed that the newly formed film took the crystal structure of the metastable  $\alpha$ -form. Thus, in this case, the transformation apparently took place by the vacuum deposition. However, the direction of the transformation turned out to be completely in the contrary way that was reported by Hamm and van Norman.

Fig. 6. is a similar film of Zn-phthalocyanine obtained by the bombardment. The selected area electron diffraction revealed rather more complicated situation. In this case, the crystal modification changed according as the locality. The fine particles which

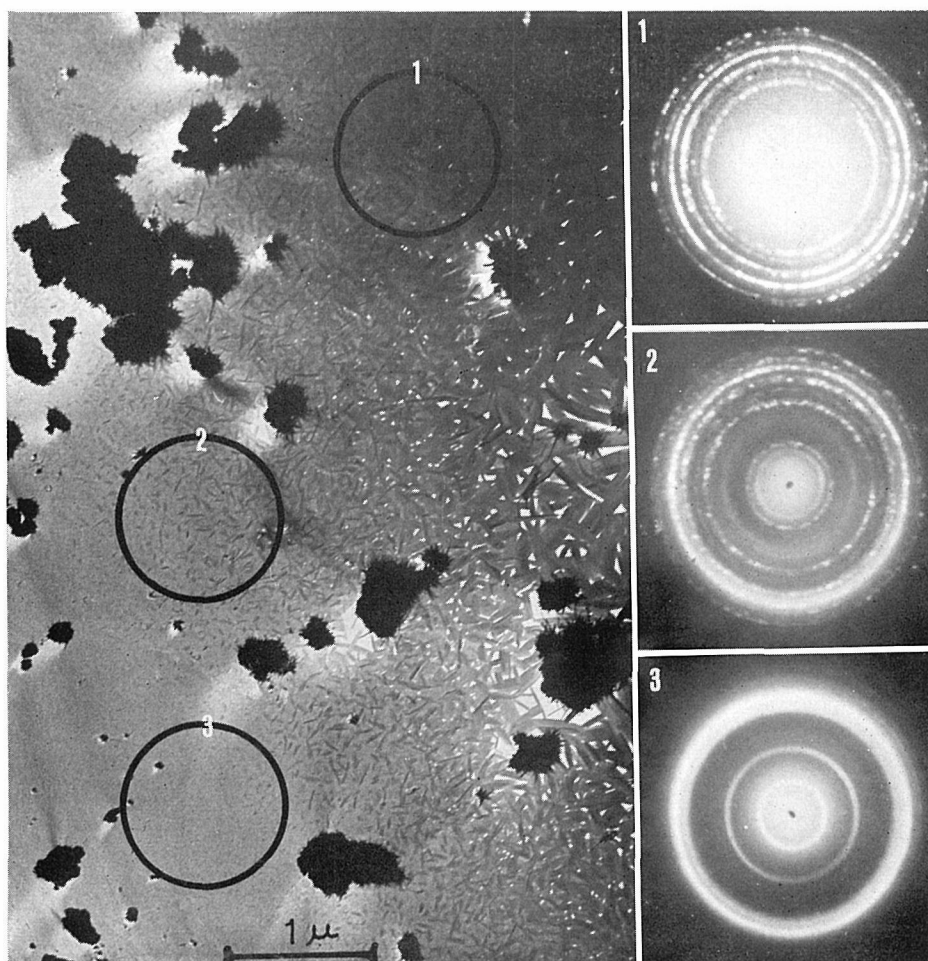


Fig. 6. Networks of Zn-phthalocyanine crystal leaf and selected area electron diffraction patterns that show the local difference of crystal structure.

appeared on the film closer to the rim of the hole (3), were identified to be the metastable crystals. However, the larger crystal strips that appeared near the center of the hole and the original crystal agglomerate, were proved to be the stable one by the analysis of the diffraction pattern 1 in the figure. The pattern 2 is simply the mixture of these two forms. Thus, in this case, it is plausible that the crystals assumed either of the two forms depending on the temperature of the substrate film. The influence of the substrate temperature upon the crystal structure of the deposited film was also reported by Karasek *et al.*<sup>6)</sup> who studied vacuum evaporated thin film of metal-free phthalocyanine on rock salt at various temperatures. By X-ray diffractometry they found that the crystals were  $\beta$ -form if the substrate temperature was higher than 200°C, which means in a way the transition temperature.

The temperature distribution of the substrate film homogeneously irradiated by electron beam was calculated by Kanaya<sup>7)</sup>. And the results are qualitatively represent-

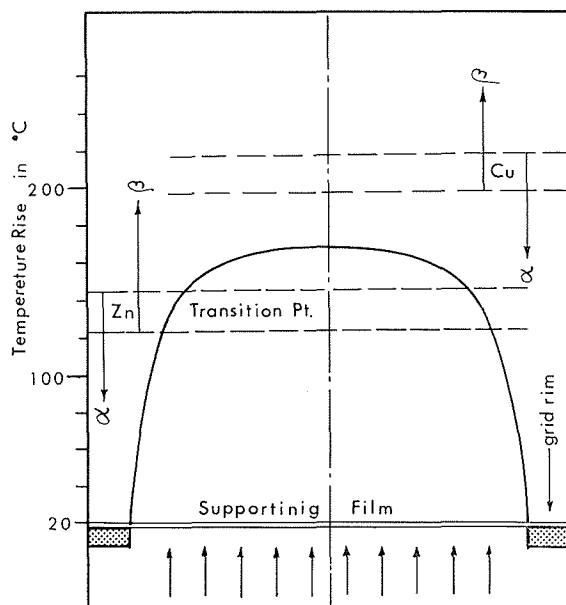


Fig. 7. Schematic diagram for the interpretation of local difference of crystal form in Zn-phthalocyanine leaves. The upright arrows show the parallel electron beam.

ed in Fig. 7. In the case of Zn-phthalocyanine, the transition point could have been lower than the maximum temperature of the film that was expected as shown in the figure. The actual value of this transition point is still uncovered and left for the further investigation. As to the case of Cu-phthalocyanine, the transition point seemed much higher than that. The lathy crystals in these networks obtained by the electron bombardment always have a great tendency to partial orientation as already pointed out with the fiber diffraction pattern in Fig. 4 B. Fig. 8 A is a spotty diffraction pattern which showed a good coincidence with the Debye-Scherrer rings in B. The latter one is also in good accordance with the high resolution pattern in Fig. 4. A cross grating pattern was distinguished from such spotty diffraction pattern by a careful analysis. However, a well-defined cross-grating was obtained from a large crystalline strip as shown in Fig. 9. With such a single crystal pattern, one can estimate the unit cell constants of the crystal. The crystal structure as well as the unit cell dimensions was reported by Robinson and Klein<sup>9)</sup> for the metastable form of Cu-phthalocyanine. Unfortunately, however, these data did not explain the present diffraction pattern. For example, they assigned two large cell constants for  $a$  and  $c$  in a tetragonal unit cell. However, a much shorter periodic distance was apparently observed in the present diffraction pattern as one of the fundamental spacings. The spacing of  $3.78 \text{ \AA}$  along the  $b$ -direction in the present cross-grating pattern is a rather common spacing for the unit cell constants of these condensed polycyclic aromatic compounds. Thus, it seems reasonable to take this value into account for the assignment of the unit cell constants of the metastable

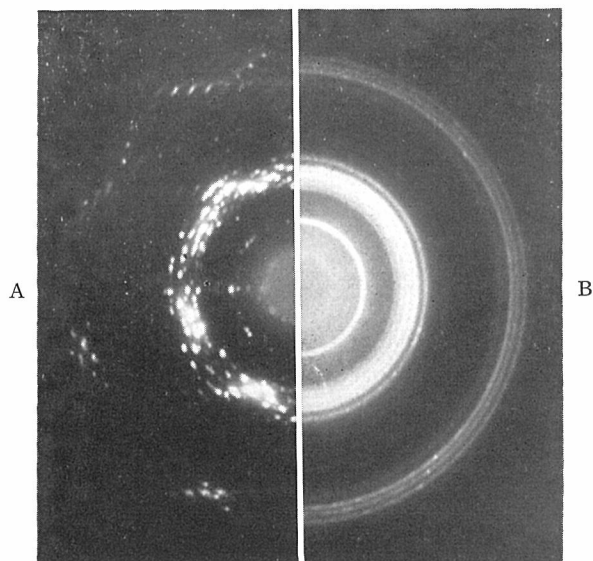


Fig. 8. Selected area electron diffraction pattern of Cu-phthalocyanine leaves obtained from (A) larger crystals area and (B) smaller crystals area both show the metastable modification.

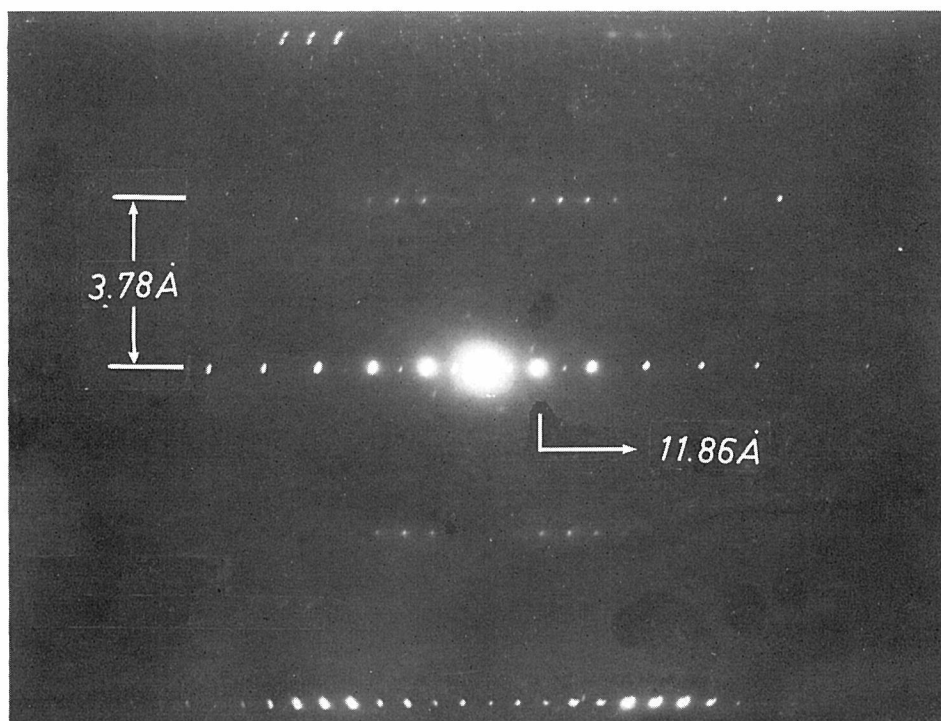


Fig. 9. Isolated single crystal pattern obtained from the similar evaporated Cu-phthalocyanine leaf.

crystal of Cu-phthalocyanine. Another fundamental spacing of 11.86 Å that appeared on the equator of the diffraction pattern is also an important value for the assignment of the unit cell. With these two values, the interplanar spacings which were collected in Table 1 were well explained.

The thin crystal strips in the networks seemed always to have the same lattice orientation, that is to say, to have a definite preferential orientation as far as the azimuthal rotation of the individual crystals is disconcerned. It was, thus, strongly anticipated that these materials would show conspicuous epitaxial growth when vacuum evaporated on some cleaved faces of single crystals. Thin vacuum deposited films of the metastable Cu-phthalocyanines were obtained on cleaved faces of muscovite with well-defined orientation<sup>9)</sup>. The crystal data obtained from this film also supported the present result concerning the cross-grating pattern obtained from the networks of evaporated leaf-like crystals of the metastable Cu-phthalocyanine. The results will appear elsewhere<sup>10)</sup>.

#### ACKNOWLEDGEMENT

This work was supported by a Grant from the Ministry of Education of Japan, which is gratefully acknowledged.

#### REFERENCES

- (1) P. B. Report, 74892 (1947), 9060; 85172 (1947) 412.
- (2) E. A. Hamm and E. van Horman, *J. Appl. Phys.*, **19**, 1097 (1948).
- (3) H. Sasaki, R. Ueda and Y. Kubota, Read at the Osaka Meeting on Electron Micros., Japan., Nov. (1951).
- (4) E. Suito and N. Uyeda, *Proc. Japan Acad.*, **32**, 182 (1956); *Kolloid-Z.*, **193**, 97 (1963).
- (5) E. Suito, N. Uyeda and M. Ashida, *Nature*, **194**, 273 (1962).
- (6) F. W. Karasek and J. C. Decius, *J. Am. Chem. Soc.*, **74**, 2807 (1952).
- (7) K. Kanaya, *J. Electronmicros.*, **3**, 1 (1955).
- (8) M. T. Robinson and G. E. Klein, *J. Am. Chem. Soc.*, **74**, 6294 (1952).
- (9) N. Uyeda, M. Ashida and E. Suito, Fifth Intern'l Congr. Electron Microscopy, Philadelphia, **1**, GG-15 (1962).
- (10) N. Uyeda, M. Ashida and E. Suito, *J. Appl. Phys.*, **36**, 1453 (1965).