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Unit Cell Metastable-form Constants of Various Phthalocyanines

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Thin films of phthalocyanine compounds formed on cleaved surfaces of muscovite by the vacuum-condensation method showed well-defined single-directional orientation when their substrates were preheated at 300°C for one hour and then kept at 150°C. Their electron diffraction patterns were fiber diagrams, the fiber period of which coincided with the unit-cell length of the b-axis of the individual compounds. When the substrates were preheated at 400°C for one hour and then kept at 150°C, the films formed on the muscovite surface were composed of discrete crystals with a different orientation. Electron-diffraction patterns from the films revealed that the b-axis of the crystal was inclined to the substrate surface. The cross-grating patterns of the $(h0l)$ plane were obtained when the inclination of the films was properly adjusted to the incident beam. The unit-cell constants of platinum-phthalocyanine vacuum-condensed on muscovite were revealed to be as follows with the monoclinic space group $C2/c$: $a=23.18$ Å, $b=3.818$ Å, $c=23.84$ Å, and $\beta=91.9°$. Films of Cu-, Co-, Fe-, Ni- and metal-free phthalocyanines exhibited an orientation similar to that of the platinum derivative. High-resolution electron-diffraction patterns revealed that all the compounds assumed a conspicuous isomorphism with one another and occurred in the metastable forms of their dimorphs.

The polymorphism of some phthalocyanine derivatives was very briefly described by German investigators[1] for the first time. Later, Hamm and van Norman[2] examined the microcrystals of copper-phthalocyanine by electron microscopy and identified the dimorphs with two different characteristic electron-diffraction patterns. Susich[3] found the polymorphs of metal-free phthalocyanine by X-ray diffraction. Wiswall[4] also referred to polymorphic pairs of copper-, nickel- and zinc-phthalocyanines. Ebert and Gottlieb[5] reported the differences in infrared absorption spectra and X-ray diffraction diagrams due to the dimorphs with respect to copper-, metal-free, cobalt-, nickel- and zinc-phthalocyanines. Furthermore, Karasek and Decius[6] observed polymorphic crystalline states of metal-free phthalocyanine by depositing a film of the material directly onto a highly-polished and relatively cool rock salt at a pressure of 10^{-5} mmHg.

Robertson[7,8] and Robertson and Woodward[9,10] extensively investigated the crystal structures of the stable forms of phthalocyanine and its metal derivatives by X-ray diffraction using single crystals which had been prepared by sublimation under a low pressure of carbon dioxide. On the other hand, the metastable forms of several phthalocyanine derivatives have been reported by many investigators, as has been mentioned above, but there is very little information available on the crystal data. The only report on the crystal data of the metastable forms was that on copper-phthalocyanine, determined by means of X-ray powder diffraction by Robinson and Klein.[11] Since the metastable form was obtained only as a fine powder, with a small tendency to form single crystals which were large enough, the accurate determination of the crystal data for the metastable form involves many difficulties when the ordinary method is used.

In a previous paper,[12] the present authors reported that films of phthalocyanine compounds vacuum-condensed on a cleaved face of muscovite epitaxialy grew when the substrate was maintained at a temperature of 150°C to 170°C. Since the films thus prepared was composed of crystals which assumed a well-defined orientation, an electron diffraction pattern obtained from the film showed a fiber or a single crystal diagram, from which the crystal axes and the cell dimensions might be

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[1] P. B. Report, 700336, p. 7945.

[2] F. A. Hamm and E. van Norman, *J. Appl. Phys.*, **19**, 1097 (1948).

[3] G. Susich, *Anal. Chem.*, **22**, 426 (1950).

[4] R. H. Wiswall, Jr., U. S. Pat. 2486351.

[5] A. A. Ebert, Jr., and H. B. Gottlieb, *J. Am. Chem. Soc.*, **74**, 2806 (1952).

[6] F. W. Karasek and J. C. Decius, ibid., **74**, 4716 (1952).

[7] J. M. Robertson, *J. Chem. Soc.*, **1935**, 615.

[8] J. M. Robertson, ibid., **1936**, 1195.

[9] J. M. Robertson and I. Woodward, ibid., **1937**, 219.

[10] J. M. Robertson and I. Woodward, ibid., **1940**, 36.

[11] M. T. Robinson and G. E. Klein, *J. Am. Chem. Soc.*, **74**, 6294 (1952).

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

determined with ease even though each crystal was very small. The present authors[13] also studied the orientation overgorwth of platinum-, copper- and zinc-phthalocyanines vacuum-condensed on muscovite by electron diffraction; they thus found that all three compounds showed a conspicuous isomorphism with one another and that copper- and zinc-phthalocyanines occurred in the metastable forms of their dimorphs. As for the metastable form of copper-phthalocyanine, the analysis of the electron diffraction pattern of the film revealed that the crystal data reported by Robinson and Klein[11] failed reasonably to explain the results on the film and that another, more appropriate crystal structure should be proposed instead. Honigmann et al.[14] studied the metastable form of copper-phthalocyanine and its chloroderivatives by X-ray diffraction and supported the present authors' proposition that the metastable form of copper-phthalocyanine was isomorphous with platinum-phthalocyanine.

When the depositing conditions were modified, another, different orientation occurred with the same metastable phase. These condensation methods were also extended to derivatives other than platinum-, copper- and zinc-phthalocyanines, which had previously been reported on. Using films which assumed two different kinds of orientation, the crystal data of the individual materials were estimated directly from the electron-diffraction pattern. In the present paper, the crystal data will be determined for the metastable forms of platinum-, copper-, cobalt-, iron-, nickel- and metal-free phthalocyanines with regard to the vacuum-condensed films by means of high-resolution electron diffraction.

Experimental

Materials.—Platinum-, copper- and metal-free phthalocyanines were supplied by the Sumitomo Kagaku Co. Cobalt-phthalocyanine was synthesized from phthalonitrile and anhydrous cobalt chloride, while iron-phthalocyanine was synthesized from phthalonitrile and anhydrous ferric chloride, by the method established by Barrett et al.[15] All of these materials were purified by repeated sublimation in a low-pressure stream of carbon dioxide at a temperature above 500°C. The products were obtained as small needle-like crystals, which were established as assuming the stable forms reported by Robertson.

The Preparation of Vacuum-condensed Films.—A 2×2 cm^2 cleaved sheet of muscovite was placed in a Pyrex glass tube, and then this tube was inserted in an electric furnace, as Fig. 1 shows. The purified material was sublimated from a conical-type heater of tungsten wire. The heater was placed in the part of the tube protruding from the furnace because of the necessity of keeping the material from sublimation during the preliminary thermal treatment of muscovite. About 2 mg. of the material was condensed vertically onto a cleaved face of muscovite in a vacuum of 5×10^{-5} mmHg. The thickness of the films was estimated to be in a range from 500 Å to 900 Å. The rate of deposition was 20—30 Å/min. The specimen for an electron microscopy was prepared by the wet-stripping method after it had been reinforced by evaporated carbon film. Thalium chloride evaporated on phthalocyanine films was used as the standard specimen for the high-resolution diffraction work.

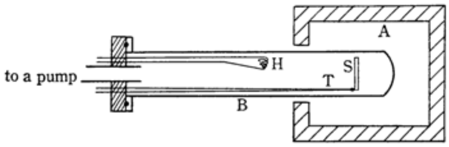

Fig. 1. Schematic diagram of appratus.
A: electric furnace, B: Pyrex glass tube
S: substrate mica sheet, T: thermocouple
H: tungsten heater (evaporation source)

The Determination of Densities.—As the quantity of the material deposited on muscovite was too small for the density to be measured, powderly crystals of the metastable form prepared by the acid-paste method[16] were used in place of the sublimated films. The densities of the materials were determined by a 5% methyl alcohol displacement in a 25 ml. pycnometer.

Results

a) Platinum-phthalocyanine.—When muscovite was preheated at 300°C for one hour and held at 150°C, the film condensed on it was composed of laminar crystal strips which parallelly grew in a definite direction, as is shown in Fig. 2(a). An electron-diffraction pattern from the film shows the fiber structure shown in Fig. 2(b). The fiber axis coincides with the longitudinal direction of the crystals, and the fiber period is 3.81 Å.

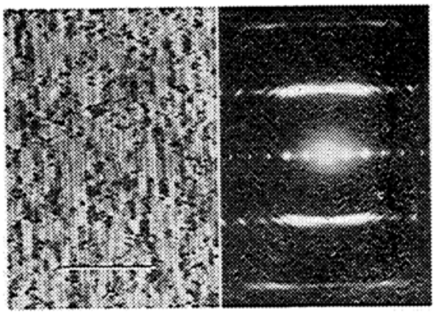
(a) (b)

Fig. 2. Electron micrograph (a) and electron diffraction pattern (b) of Pt-phthalocyanine film vacuum-condensed on muscovite which is preheated at 300°C and kept at 150°C.

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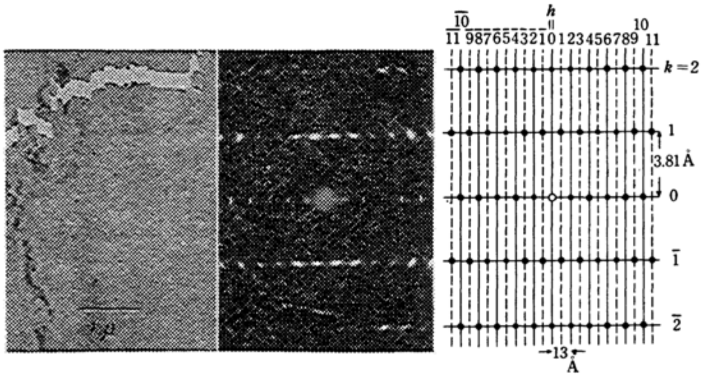
13) N. Uyeda, M. Ashida and E. Suito, *J. Appl. Phys.*, **36**, 1453 (1965).

14) B. Honigmann, H. Lenne and R. Schrödel, *Z. Krist.*, **122**, 185 (1965).

15) P. A. Barrett, C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, **1936**, 1719.

16) E. Suito and N. Uyeda, *Kolloid-Z.*, **193**, 97 (1963).



(a) (b)

Fig. 3. Electron micrograph (a) and electron diffraction pattern (b) of single crystal film of Pt-phthalocyanine and its schematic diagram (c).

On the equator, two sets of reflection spots simultaneously appeared, corresponding to an interplanar spacing of 13.1 Å and 11.9Å. As has been reported previously[13] the appearance of the two sets of equatorial reflection spots indicates that the film consists of at least two kinds of crystal strips with different lattice orientations. The crystal structure of platinum-phthalocyanine determined by Robertson has the following unit-cell dimensions with the monoclinic space group $P2_1/a$: $a=23.9$ Å, b=3.81 Å, b=16.9 Å, and $\beta=129.6°$. Since the fiber period obtained from the diffraction pattern showed a good coincidence with the unit lentgth of the b-axis, the b-axis of the crystal strips turned out to be parallel to the longitudinal direction. As for the two characteristic reflections on the equator, the spacings of 13.1 Å and 11.9 Å corresponded to the (001) and (20$\bar{1}$) planes respectively, planes which are almost perpendicular to each other and which share the b-axis as the zone axis. However, a closer observation of the electron diffraction pattern revealed that it was necessary to reconsider the designation of the crystal axes. A perfect single crystal was obtained in the part of the film prepared as above. Figs. 3(a) and (b) show respectively, an electron micrograph and electron diffraction pattern from the film. In Fig. 3(b), the maximum lattice period along the meridian is 3.81 Å, which is the same value as that of the fiber diagram. On the other hand, the period of 13.1 Å in the equatorial direction corresponded to 001 and its higher-order reflections, according to Robertson's assignment. This means that the diagram shows the reciprocal lattice plane with the index of 0*kl*. However, when the reflection spots appearing on the lines of $k=1$ and 3 are taken into account, it is obvious that the period along the equator should take twice as long as that given by Robertson by adding the periods displayed to the broken lines in Fig. 3(c). If the equator is identified as the a* axis of the reciprocal lattice, then all the reflection spots in Fig. 3(b) may be indexed as in Fig. 3(c). The possible reflection is as follows: *h* is even in (*h*00), *k* is even in (0*k*0), and $k+k$ is even in (*hk*0).

When a muscovite substrate was preheated at 400°C for one hour and kept at 170°C, the film condensed on it was composed of discrete crystallites, as Fig. 4(a) shows. The electron-diffraction pattern in Fig. 4(b) is apparently a superposition of two identical diagrams, both composed of layered zones of reflection spots. The appearance of these layered zones in the individual diagrams is to be ascirbed to the position of the main-zone axes of the sublimated crystal, which tilts against the substrate face and consequently against the electron beam. The orientation will be described in detail in another report. However, it must be noted here that the crystallites are divided into

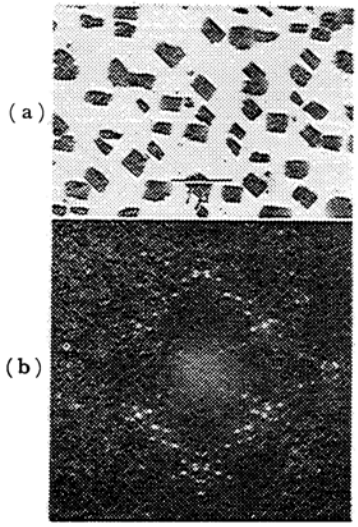


Fig. 4. Electron micrograph (a) and electron diffraction pattern (b) of Pt-phthalocyanine film vacuum-condensed on muscovite which is preheated at 400°C and kept at 170°C.

two groups, which can be defined by a plane of symmetry, normal with regard to the total film plane, as far as the lattice orientation is concerned. The b-axis stands somewhat obliquely to the film plane. Therefore, when the film is tilted against the incident electron beam so that the b-axis of the crystal becomes parallel to the beam, the intensity distribution of the reflection spots is symmetrized with respect to the point of origin, as is shown in Fig. 5. As the incident beam is parallel to the b-axis of the crystal, the diagram shows the reciprocal lattice points with the $h0l$ indices. Since the b-axis of the crystals taking another orientation does not become parallel to the incident beam, and since the unit length of the b* reciprocal axis is considerably longer than those of the a* and c* axes, the reflection from these crystals of another group gave rise to only a few extra spots, indicated with arrows in the figure. The cross-grating pattern consisted of two arrays of reflection spots, with periods of 13.1 Å and 11.9 Å, which cross each other at an angle of 88.1°. Since the interplanar spacings agreed with those obtained from the fiber diagram, both crystals were assigned the same structure. When the a* axis of the reciprocal lattice was associated with the period of 13.1 Å described above, the c* axis was to be ascribed to the other period, 11.9 Å. The unit lengths of a- and c-axes and the axial angle, β, were directly obtained from the pattern. The possible reflection was as follows: both h and l are even in ($h0l$). Although these possible reflections in ($h00$), ($0k0$), ($hk0$) and ($h0l$) appear in both space groups, C_s^4–C_c and C_{2h}^6–$C\,2/c$, it is well known that platinum-phthalocyanine is a planar molecule which has a center of symmetry. On the basis of these results, the unit cell constants were determined to be as given in Table I (1). As has been mentioned above, the new designation of the crystal axes was given by the substitution of (200) and (002) respectively for the (001) and ($20\bar{1}$) planes assigned by Robertson.

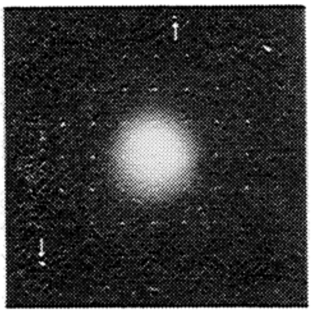


Fig. 5. Electron diffraction pattern of ($h0l$) plane of Pt-phthalocyanine obtained by tilting the film shown in Fig. 4.

On the basis of such a transformation of the

Table I. Unit cell constants of Pt-phthalocyanine

	(1)	(2)	Cf. Robertson's data
a	26.18 Å	26.2 Å	23.9 Å
b	3.818 Å	3.81 Å	3.81 Å
c	23.84 Å	23.9 Å	16.9 Å
β	91.9°	95.1°	129.6°
Space group	$C_{2h}^6=C2/c$	$C_{2h}^6=C2/c$	$C_{2h}^5=P2_1/a$
Mols. per cell	4	4	2
d(calcd.)	1.96	1.97	1.97
d(found)	1.94	1.98	1.98

(1): Obtained from the crystal vacuum-condensed on muscovite,

(2): Correction of Robertson's data.

Table II. Interplanar spacings of Pt-phthalocyanine vacuum-condensed on muscovite

d(Å)	(1) I/I_0	(hkl)	(2) d(Å)	(3) d(Å)
13.12	vs.	200	13.09	13.1
11.99	s.	002	11.92	11.9
9.14	w.	$20\bar{2}$	8.965	9.19
8.43	w.	202	8.668	8.49
6.56	s.	400	5.545	6.56
5.96	s.	004	5.960	5.95
5.61	m.	$20\bar{4}$	5.495	5.60
4.62	w.	$40\bar{4}$	4.483	4.60
4.37	w.	600	4.363	4.37
4.19	vw.	$60\bar{2}$	4.143	4.21
4.01	vw.	602	4.054	4.00
3.78	m.	110	3.778	3.78
3.62	m.	$11\bar{2}$	3.607	3.61
3.41	m.	$11\bar{3}$	3.419	3.41
3.28	vw.	800	3.272	3.28
3.21	vw.	$31\bar{3}$	3.218	3.22
3.03	m.	$31\bar{4}$	3.035	3.03
2.99	vw.	314	2.999	2.99
2.95	m.	115	2.954	2.95
2.86	vw.	513	2.857	2.86
2.61	vw.	$71\bar{2}$, 316	2.609	2.61
2.52	vw.	117	2.524	2.52
2.46	w.	317	2.457	2.46
2.33	w.	$71\bar{5}$	2.353	2.33
2.17	vw.	119	2.164	2.17
2.11	vw.	$31\bar{9}$	2.126	2.11
1.99	w.	519	1.990	1.99
1.91	w.	020	1.909	1.91
1.85	vw.	023	1.86	1.86
1.76	w.	225	1.76	1.76
1.70	w.	226	1.70	1.70
1.65	vw.	426	1.65	1.65

(1): Observed values from the film vacuum-condensed on muscovite.

(2): Calculated values from the crystal data (1) in Table I.

(3): Calculated values from the crystal data (2) in Table II crystal axes, the original crystal data reported by Robertson should be corrected as in Table I (2). When the values in the column (1) are compared with those in the column (2), the coincidence is fairly good except for the value of the axial angle, β. The interplanar spacings evaluated from the fiber diagram are given in Table II (1). Tables II (2) and (3) show the interplanar spacings calculated from the cell constants given in Tables I (1) and (2) respectively. In Table II, the values in the column (2) agreed with those in the column (1) except for sevsral spacings, which had the index of $(h0l)$. These discrepancies were apparently caused by the difference in the axial angle, β, which will be discussed in a latter section.

b) Copper-phthalocyanine.—In the case of copper-phthalocyanine, films showed a fiber structure similar to that of platinum-phthalocyanine when the substrate muscovite was preheated at 300°C for one hour and held at 150°C during the vacuum-deposition. Figures 6(a) and (b) show the electron micrograph and electron-diffraction pattern of the film respectively. The fiber period was 3.79 Å, and the two sets of equatorial reflections had periods of 13.0 Å and 11.9 Å in Fig. 6(b). Since these values were quite similar to those of the platinum derivative, the crystal of vacuum-condensed copper-phthalocyanine film was ac-accounted for in terms of the isomorph with the platinum derivative. Consequently, it seems reasonable to assign the fiber period and the two long periods on the equator for the principal axial lengths of copper-phthalocyanine in the same way as for the platinum derivative.

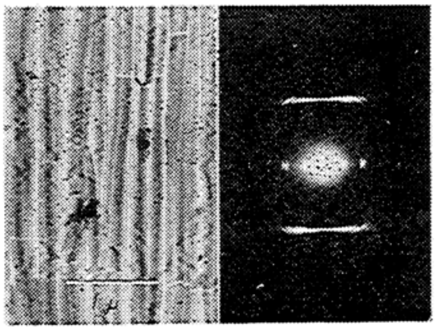

(a) (b)

Fig. 6. Electron micrograph (a) and electron diffraction pattern (b) of Cu-phthalocyanine film vacuum-condensed on muscovite which is preheated at 300°C and kept at 150°C.

Films sublimated onto muscovite which had been preheated at 400°C for one hour and held at 150°C were composed of many small crystals, as Fig. 7(a) shows. The electron-diffraction pattern from the film revealed that the b-axis of the crystals stood obliquely on the substrate face in a way similar to that of the platinum derivative. When the film was tilted against the incident beam so that the b-axis of the crystals became parallel to it, the electron diffraction pattern gave the cross-grating pattern of the $(h0l)$ plane shown in Fig. 7(b). In the cross-grating pattern, the interplanar spacings with the periods of 12.9 Å and 11.9 Å, which cross each other at the angle of 89.6°, agreed with those of the two sets of reflections on the equator in the fiber diagram. Since the crystal was found to be the isomorph of the platinum derivative, the reflection spots should be indexed in the same way. Conseuqenctly, the cell constants of the copper-phthalocyanine vacuum-condensed on muscovite were determined to be as given in Table III (1). The interplanar spacings in Table IV (I) were obtained from the fiber diagram, while those in Table IV (2) were calculated from the cell constants given in Table III (1). The values in two series showed good

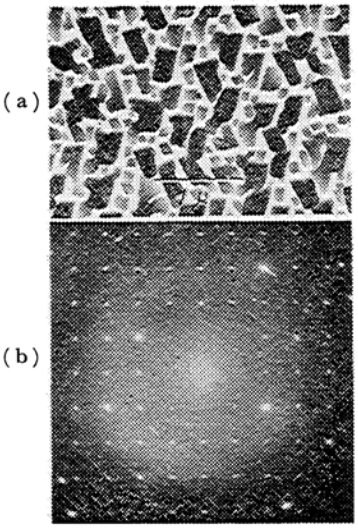


Fig. 7. Electron micrograph (a) of Cu-phthalocyanine film vacuum-condensed on muscovite which is preheated at 400°C and kept at 150°C and electron diffraction pattern (b) of $(h0l)$ plane of Cu-phthalocyanine obtained by tilting the film (a).

TABLE III. UNIT CEEL CONSTANTS OF METASTABLE FORM OF CU-PHTHALOCYANINE

	(1)	(2)
	$a=25.92$ Å	$a=25.92$ Å
	$b=3.790$ Å	$b=3.790$ Å
	$c=23.92$ Å	$c=24.10$ Å
	$\beta=90.4°$	$\beta=90.4°$
Space group	$C^6_{2h}=C2/c$	$C^6_{2h}=C2/c$
Mols. per cell	4	4
d(calcd.)	1.62	1.605
d(found)		1.62

(1): Film vacuum-condensed on muscovite.
(2): Powder prepared by acid paste method.

agreement. It was found that the crystal vacuum-condensed onto muscovite was the same metastable form as that prepared by the acid-paste method.[16] The interplanar spacings in Table IV (3) were obtained from the latter crystal by X-ray diffractometry. As each value in this column agrees well with those in the columns (1) and (2), each spacing may reasonably be indexed as in the column (3). Reversely, on the basis of the index, the cell constants were calculated from the values in Table IV(3) to be as given in Table III(2). They showed good agreement with those obtained from the vacuum-condensed film.

c) Other Phthalocyanines. — Vacuum-condensed films of iron-, cobalt-, metal-free and nickel-phthalocyanines also assumed the single directional orientation similar to that of the platinum derivative, as Figs. 8(a), (b), (c) and (d) respectively show. Figures 9(a), (b), (c) and (d) are, respectively, the electron diffraction patterns from these films. The fiber periods of these diagrams were in the range from 3.5 to 3.8 Å, and two sets of reflection spots appeared on the equator at definite intervals for each set. The findings suggest

TABLE IV. INTERPLANAR SPACINGS OF Cu-PHTHALOCYANINE VACUUM-CONDENSED ON MUSCOVITE AND PREPARED BY ACID PASTE METHOD (in Å)

$d(1)$	I/I_0	$d(2)$	(hkl)	$d(3)$	I/I_0	$d(4)$
13.01	vs.	12.96	200	12.96	vs.	12.96
11.90	s.	11.96	002	12.05	vs.	12.05
			202	8.817	m.	8.816
6.48	s.	6.480	400			
5.99	m.	5.980	004			
5.64	w.	5.678	402	5.671	w.	5.681
			$20\bar{4}$	5.479	w.	5.478
4.32	m.	4.320	600			
			602	4.068	w.	4.067
4.01	w.	3.989	006			
3.77	w.	3.750	110			
3.68	m.	3.705	$11\bar{1}$	3.704	m.	3.706
3.59	m.	3.579	$11\bar{2}$	3.560	m.	3.580
3.40	m.	3.395	$11\bar{3}$			
3.33	m.	3.336	312	3.338	m.	3.338
3.22	m.	3.186	313	3.233	m.	3.233
2.97	m.	2.967	512			
2.93	w.	2.950	115			
2.85	w.	2.853	513			
2.59	w.	2.589	712			
2.52	w.	2.525	117			
2.41	w.	2.423	317			
1.89	w.	1.895	020			

(1): Observed values from the film vacuum-condensed on muscovite
(2): Calculated values from the crystal data (1) in Table III
(3): Observed values from powder prepared by acid paste method
(4): Calculated values from the crystal data (2) in Table III

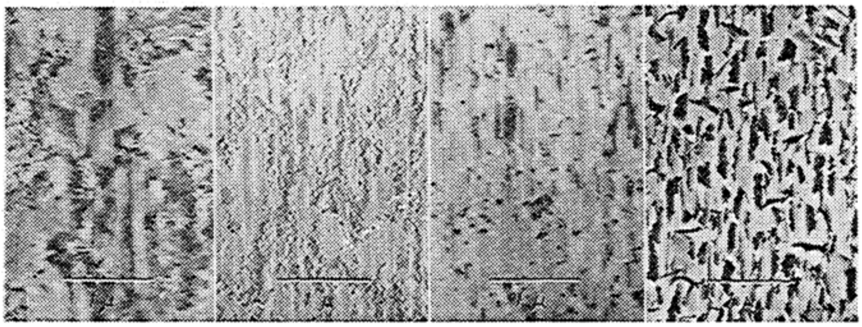
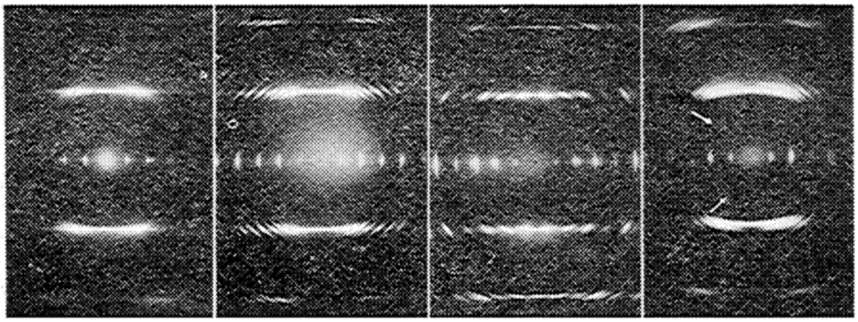
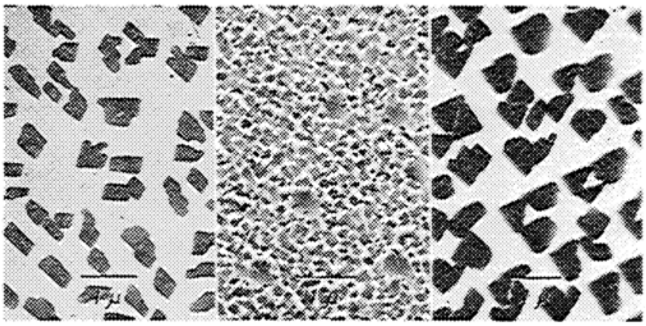

(a) (b) (c) (d)

Fig. 8. Electron micrographs of (a) Fe-, (b) Co, (c) metal-free and (d) Ni-phthaloyanine films vacuum-condensed on muscovite which is preheated at 300°C and kept at 150°C



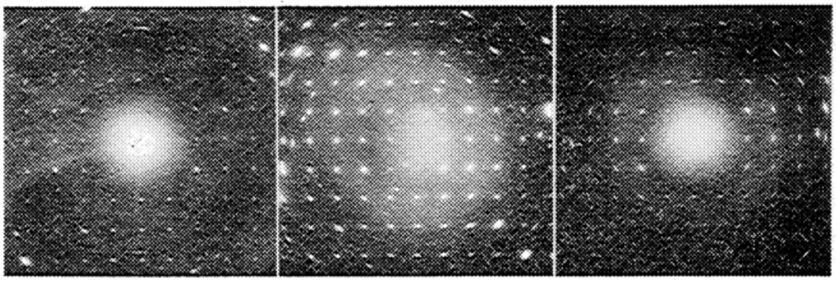
(a) (b) (c) (d)

Fig. 9. Electron diffraction patterns of (a) Fe-, (b) Co-, (c) metal-free and (d) Ni-phthalocyanine films vacuum-condensed on muscovite which is preheated at 300°C and kept at 150°C.



(a) (b) (c)

Fig. 10. Electron micrographs of (a) Fe-, (b) Co- and (c) metal-free phthalocyanine films vacuum-condensed on muscovite which is preheated at 400°C and kept at 150°C.



(a) (b) (c)

Fig. 11. Electron diffraction patterns of (*h*0*l*) plane of (a) Fe-, (b) Co- and (c) metal-free phthalocyanines obtained by tilting the films shown in Fig. 10, respectively.

not only that all four compounds occur in the metastable forms of their dimorphs, but also that they are conspicuously isomorphic with the platinum derivative. Table V shows the interplanar spacings evaluated from these fiber diagrams.

When the substrate muscovite was preheated at 400°C for one hour and then maintained at a temperature of 150°C to 200°C for the deposition, the films of iron-, cobalt- and metal-free phthalocyanines were composed of small crystals, the b-axis of which stood obliquely on the substrate face, as Figs. 10(a), (b) and (c), respectively, show. The cross-grating patterns of their (*h*0*l*) planes were obtained from the films exhibited in Figs. 11(a), (b) and (c) when these films were tilted against the incident beam in a way similar to that used with the platinum derivative. The unit lengths of the b-axes of these phthalocyanines were obtained from the fiber diagrams, while the unit lengths of the a- and c-axes and the axial angle, β, were determined from the cross-grating patterns. The unit cell constants were determined to be as given in Table VI for the metastable forms of these phthalocyanines; in the table the unit cell constants of platinum- and copper-phthalocyanines are again reproduced for the sake of reference. When the

Table V. Interplanar spacings of Fe-, Co-, Ni- and metal-free phthalocyanines vacuum-condensed on muscovite

	Fe-Pc			Co-Pc			H_2-Pc			Ni-Pc		
(*hkl*)	*d*(o)*	*I*	*d*(c)**	*d*(o)	*I*	*d*(c)	*d*(o)	*I*	*d*(c)	*d*(o)	*I*	*d*(c)
200	13.1	vs.	12.95	12.9	vs.	12.94	13.1	s.	13.07	13.06	s.	13.07
002	12.5	vs.	12.05	12.6	vs.	12.04	11.9	vs.	11.98	12.12	vs.	12.13
202										8.54	w.	8.544
400	6.55	s.	6.535	6.47	s.	6.470	6.56	s.	6.535	6.56	m.	6.535
004	6.05	s.	5.990	6.27	s.	6.020	5.96	vs.	5.990	6.06	s.	6.065
$20\bar{4}$										5.68	m.	5.688
204										5.34	w.	5.334
600	4.34	m.	4.360	4.32	m.	4.311	4.35	m.	4.360	4.36	m.	4.357
006	4.13	vw.	3.993	4.18	w.	4.013	3.97	w.	3.993	4.05	m.	4.043
110	3.72	m.	3.726	3.72	m.	3.711	3.77	m.	3.774	3.77	m.	3.751
$11\bar{1}$				3.66	w.	3.668	3.73	w.	3.730	3.68	m.	3.713
$11\bar{2}$	3.58	m.	3.560	3.56	w.	3.547	3.61	s.	3.603	3.56	w.	3.571
310	3.49	s.	3.451	3.43	m.	3.439						
311	3.43	vw.	3.416									
$11\bar{3}$	3.39	vw.	3.380	3.36	vw.	3.369	3.42	s.	3.416			
800	3.25	vw.	3.267	3.25	vw.	3.235	3.25	vw.	3.267	3.24	s.	3.267
313	3.17	w.	3.171	3.15	w.	3.160	3.20	m.	3.210	3.19	s.	3.173
510	3.07	w.	3.046	3.05	w.	3.038				3.05	vw.	3.068
$11\bar{5}$	2.95	vw.	2.949	2.96	vw.	2.948	2.97	m.	2.967			
513	2.89	m.	2.848	2.88	w.	2.842	2.84	w.	2.864	2.82	w.	2.823
$71\bar{2}$	2.63	w.	2.578	2.58	vw.	2.573	2.59	w.	2.612			
117	2.51	vw.	2.529	2.49	vw.	2.500						
317				2.45	w.	2.433				2.43	vw.	2.417
$71\bar{5}$				2.33	vw.	2.313						
518				2.14	vw.	2.136	2.17	w.	2.173			
519				1.99	vw.	2.005						
020	1.88	w.	1.883	1.87	w.	1.875	1.91	w.	1.907			
023	1.84	w.	1.833	1.82	vw.	1.826	1.84	w.	1.855			

* *d*(o): observed value ** *d*(c): calculated value

Table VI. Unit cell constants of various phthalocyanines vacuum-condensed on muscovite

	Pt-Pc	Cu-Pc	Fe-Pc	Co-Pc	Ni-Pc	H_2-Pc
a	26.18 Å	25.92 Å	25.90 Å	25.88 Å	26.15 Å	26.14 Å
b	3.818 Å	3.790 Å	3.765 Å	3.750 Å	3.790 Å	3.814 Å
c	23.84 Å	23.92 Å	24.10 Å	24.08 Å	24.26 Å	23.97 Å
β	91.9°	90.4°	90.0°	90.2°	94.8°	91.1°
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
d(calcd.)	1.96	1.62	1.59	1.61	1.57	1.42
d(found)	1.94	1.62		1.65	1.62	1.44

fiber diagram was compared with the cross-grating pattern, the interplanar spacings which are associated with two sets of reflections on the equator were found to be 13.1 Å and 12.5 Å for the iron derivative, and 12.9 Å and 12.5 Å for the cobalt derivative, while the periods corresponding with these reflections in the cross-grating patterns were 12.9 Å and 12.05 Å for the former and 12.94 Å and 12.04 Å for the latter. In the cases of iron- and cobalt-phthalocyanines, therefore, the interplanar spacings calculated from the unit cell constants given in Table VI showed a discrepancy of about 4% from those obtained with the fiber diagrams. No serious difference was observed in metal-free phthalocyanine.

In the case of nickel-phthalocyanine, extra spots always appeared between the equator and the first-layer line in the fiber diagram, as is shown with arrows in Fig 9(d). The film was composed of laminar crystal strips, giving rise to a raft structure as a whole, and beard-like crystals appearing among the raft structure, as Fig. 8(d) shows. The reflections from the former crystals produced the fiber pattern, while those from the latter crystals appeared as extra spots. As for the nickel derivative, no films which showed another orientation were obtained. In the fiber diagram, the maximum lattice period along the meridian was 3.79 Å and the interplanar spacings were 13.07 Å and 12.13 Å, these spacings are associated with two sets of reflections on the equator. Since these values were very similar to those of other phthalocyanines, the interplanar spacings obtained from the fiber diagram were indexed as in Table V. The unit-cell constants of nickel-phthalocyanine given in Table VI were then calculated from the interplanar spacings thus indexed.

Discussion

Robertson⁷⁾ and Linstead and Robertson¹⁷⁾ reported that metal-free, beryllium-, manganese-, iron-, cobalt-, nickel- and copper-phthalocyanines were isomorphic and that the unit lengths of their b-axis fell in the range from 4.71 Å to 4.84 Å, and that only the platinum-phthalocyanine had the unit length of the b-axis of 3.81 Å and was not isomorphic with the others. As is well known, however, their investigations were restricted to the stable forms of these compounds; no account was taken of the metastable form. Honigmann et al.¹⁴⁾ suggested that the individual unit cells of phthalocyanine compounds should contain four molecules and that, considering its isomorphic behavior with other phthalocyanine derivatives, the space group of platinum-phthalocyanine was transformed into $B2_1/a$. However, the space group assigned by them was based on the molecular orientation reported by Robertson and Woodward.¹⁰⁾ Recently, Brown¹⁸⁾ proposed that the space group of platinum-phthalocyanine should be corrected by means of a new interpretation that $C2/c$ of the monoclinic system is more plausible, since it is twice as large as that reported by Robertson. His proposition coincides well with the crystal data reported in the present paper. Consequently, it may be concluded that the unit cell constants of platinum-phthalocyanine should be transformed to those give in Table I(2). In Table II, the values in the column (1) agreed well with those in (2). On the other hand, there were small discrepancies between the values in (3) and those in (1) and (2) as a result of the difference in the axial angle, β. The result shows that the laminar crystals which assume the single directional orientation have the same structure as that investigated by Robertson, while the crystals which have the b-axis standing obliquely on the substrate face are distorted from the original structure, possibly because of the bond forces between the deposited crystal and the substrate muscovite.

As for the metastable form of copper-phthalocyanine prepared by the acid-paste method, Robinson and Klein reported the crystal to be $P4/m$ of the tetragonal system with the following unit cell constants: $a=17.376$ Å and $b=12.790$ Å.¹¹⁾ This crystal, however, unfortunately cannot explain the present results which are directly obtained by electron diffraction. It should be reasonable to take the lattice spacing of 3.79 Å into consideration in determining the basic configuration of the unit cell, not only because the fiber diagram of the diffraction requires them, but also because this spacing is nearest the case of platinum-phthalocyanine and some other condensed polycyclic aromatic compounds.¹⁹⁾ The cell constants represented in this paper were confirmed with the results obtained by X-ray diffraction.

In the cases of iron- and cobalt-phthalocyanines, the unit length of the c-axis showed a discrepancy of less than 4% between the value obtained from the fiber diagram and that obtained from the cross-grating pattern. This discrepancy may be caused by the lattice distortion of the deposited crystal, which is accompanied by a slight change in the molecular arrangement in the crystal due to the lattice orientation relative to the substrate muscovite. Consequently, except for copper- and platinum-phthalocyanines, which were confirmed with a crystal prepared by another method, the crystal data obtained from the vacuum-condensed films may be expected to show some deviation. In spite of such possible deviations, however, it is believed that these crystal data are very useful for the study of the metastable form of phthalocyanine compounds because the metastable form of phthalocyanine compounds have not yet been obtained in the large, single-crystalline state from which the crystal data were determined by X-ray diffraction.

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17) R. P. Linstead and J. M. Robertson, *J. Chem. Soc.*, **1936**, 1736.

18) C. J. Brown, Private communication (1966).

19) H. Akamatu and K. Nagamatsu, *J. Colloid Sci.*, **2**, 593 (1947).