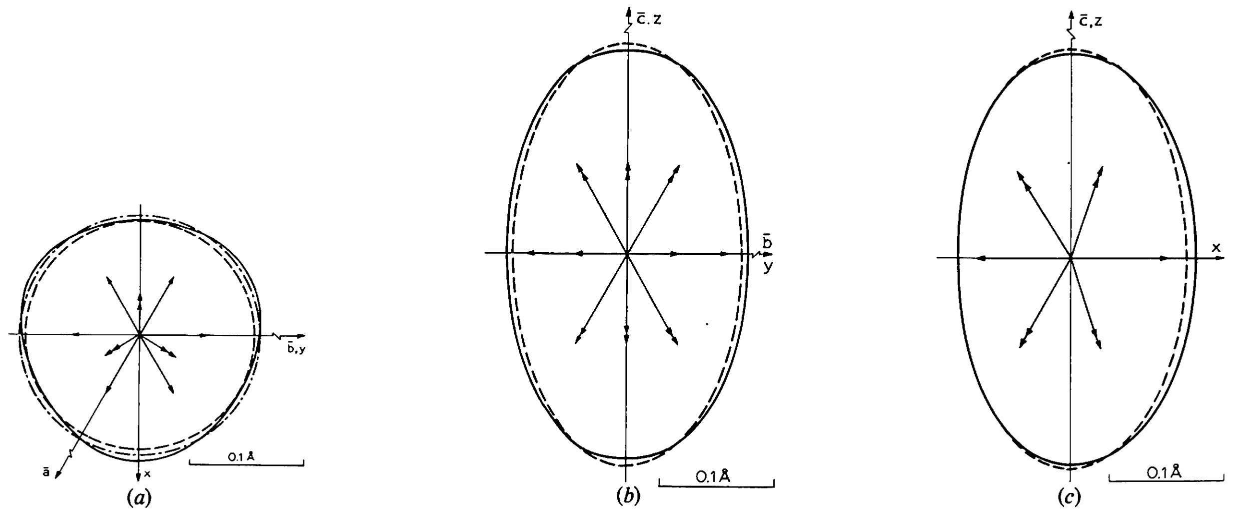

Fig. 2. Equipotential contours [$V(\mathbf{u}) = 0{\cdot}025 \times 10^{-19}$ J] in Zn, (*a*) in the basal plane, (*b*) in *yz* plane (plane perpendicular to a mirror plane), (*c*) in *xz* plane (a mirror plane). Arrows with one tip are the direction indicators or their projections of the nearest neighbours, arrows with two tips are those of the next-nearest neighbours (*cf.* Fig. 1). Dashed lines are obtained by including only the harmonic terms, dash-dotted lines by adding the quartic terms, and the solid line by adding both cubic and quartic terms to the one-particle potential function.

The section of equipotential surfaces in the *yz* plane (perpendicular to the atomic mirror plane) shown in Fig. 2(*b*) illustrates the symmetric distortion of the effective one-particle potential function due to the quartic terms (contribution of the third order term is now identically zero). Fig. 2(*c*) shows the combined influence of the symmetric and antisymetric distortions in a mirror plane.

The study of thermal vibrations in Zn is being pursued by neutron single crystal studies at a number of elevated temperatures.

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# Molecular Images of Thin-Film Polymorphs and Phase Transformations in Metal-Free Phthalocyanine

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## Abstract

Molecular imaging of metal-free phthalocyanine, prepared expitaxically on KCl, showed two polymorphs. The unit-cell constants, measured from the *ac* projection, differed from previously quoted values and this was attributed to the effect of the preparation substrate. The transformation of one phase into another was apparently martensitic with lamellae of the opposite phase being present in both polymorphs.

Polymorphism is a common phenomenon in molecular crystals and the existence of polymorphs of phthalo-

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cyanine $C_{32}H_{18}N_8$ (Fig. 1) has been extensively investigated. A major source of interest has been promoted by the use of phthalocyanine as a blue pigment, but more recently its semiconductor properties have received attention. One difficulty with phthalocyanine, and its metal derivatives, has been that crystal growth from solution only produces the stable phase under conditions suitable for giving crystals of a size convenient for X-ray structure analysis. The metastable polymorphs can only be obtained under rapid growth conditions where the product consists of very small crystals. Examples of these rapid conditions are vacuum condensation of the vapour on to various substrates and precipitation by rapid aqueous dilution of solutions of phthalocyanines in concentrated sulphuric acid (known as 'acid pasting'). Therefore structural characterization of the metastable polymorphs has either used powder X-ray techniques or electron diffraction in the electron microscope – neither of which are as accurate as single-crystal X-ray methods. In this work is described the application of molecular imaging, using minimal exposure techniques, to thin films of phthalocyanine prepared by evaporation on to heated KCl. The unit-cell dimensions can be measured directly from the micrographs and compared with electron diffraction measurements.

The structure of the stable $\beta$ phase of phthalocyanine was determined by Robertson (1935) and shown to be similar to the copper, nickel and platinum derivatives in having a space group of $P2_1/a$ with two molecules in the unit cell. The unit-cell dimensions were $a = 19{\cdot}85$, $b = 4{\cdot}72$, $c = 14{\cdot}8$ Å and $\beta = 122°\,15'$. Subsequently this was modified by Donnay & Donnay (1963) in that they quote $a = 17{\cdot}3$ Å and $\beta = 104°\,41'$ with agreement on the other values. Three polymorphs of phthalocyanine were reported by Susich (1950) and differentiated by X-ray powder photographs but a more detailed examination was carried out by Ebert & Gottlieb (1951) who detected only two polymorphs using both X-ray and infrared absorption techniques. Karasek & Decius (1952) prepared the $\alpha$-phthalocyanine (metastable form) by evaporation on to polished NaCl maintained below 473 K in a vacuum of $7{\cdot}6 \times 10^{-8}$ Pa. The $\beta$ form was obtained if the substrate temperature was raised to 673 K. A similar preparation technique was used by Ashida, Uyeda & Suito (1966) with a muscovite substrate in an extensive study of phthalocyanine and its copper, iron, nickel, platinum and cobalt derivatives. The metastable phthalocyanine was prepared and found to be isomorphous with its metal derivatives in their metastable forms. Furthermore a better description of the space group was $C2/c$ giving the following unit-cell constants for the $\alpha$-phthalocyanine: $a = 26{\cdot}14$, $b = 3{\cdot}814$, $c = 23{\cdot}97$ Å, $\beta = 91°\,6'$ with four molecules in the unit cell. The authors attributed the differences between their constants and the previously published values – corrected to a $C2/c$ space group – to lattice distortions caused by the substrate crystal. More recently, molecular imaging has shown that metastable ($\alpha'$) copper phthalocyanine is not isomorphous with the platinum derivative (Murata, Fryer & Baird, 1976*a*).

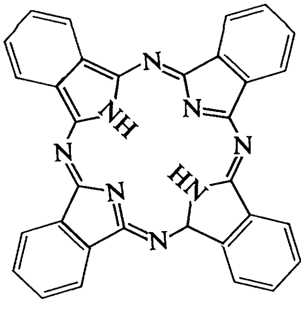
Fig. 1. Molecular structure of phthalocyanine.

A high-pressure phase of phthalocyanine was isolated by Kirk (1967) who found a reversible transformation occurred at $7{\cdot}2 \times 10^{-2}$ Pa giving a monoclinic structure of $a = 23{\cdot}7$, $b = 3{\cdot}91$, $c = 16{\cdot}1$ Å and $\beta = 130°$ whilst Vidadi, Chistyakov & Rosenshtein (1969) detected a change in the dielectric constant of evaporated thin films exposed to air at room temperature. This change was attributed to a spontaneous phase transformation and though this suggestion was not subjected to structural confirmation, it is indicative of the lability of either the molecules or the charges in this material.

The application of molecular imaging to molecular crystals has been restricted by the sensitivity of organic molecules to the radiation damage caused by the electron beam. The radiation dose for total disruption of phthalocyanine has been measured as $3{\cdot}7 \times 10^{11}$ Bq $s^{-1}$ $mm^{-2}$ at 60 keV (Reimer, 1960) which is approximately ten times less than the dose for the copper derivative that has been studied (Murata, Fryer & Baird, 1976*a*). This stability is comparable with that of naphthacene and hydrocarbons of this order of stability have been imaged at 100 keV (Fryer, 1978). In the images of such sensitive specimens it was not expected that details of molecular shape would be resolved, but the arrangement of the molecules in terms of point centres would identify the crystallographic phase provided the specimen was viewed in the appropriate projection. The planar phthalocyanine molecules are superimposed in columns as shown in Fig. 2. A view down the column axis – the *b* axis – shows the *ac* projection. The separation of adjacent molecular columns is approximately 10–15 Å and such periodicities are relatively insensitive to defocus. Thus, molecular positions could be identified in images that were taken at defocus increments that were different from the Scherzer defocus. The minimal-exposure technique tends to produce micrographs of variable defocus increments because of undulations in the specimen support film. In this particular study small variations in defocus ($< \pm 1000$ Å) produced molecular images in both white and black contrast. The prepared films were very thin, so that dynamical scattering effects were not significant, therefore either contrast was sufficient to indicate molecular positions.

## Experimental

Resublimed phthalocyanine was evaporated on to cleaved KCl. The KCl crystals were preheated in vacuum at 673 K for 1 h and maintained at 493 K during evaporation. The vacuum was $7{\cdot}6 \times 10^{-8}$ Pa. The thin evaporated film was backed with a thin film of evaporated carbon to provide mechanical strength and floated off the KCl crystal on to water where it was picked up on a flat 400-mesh grid.

The specimen was examined in a JEOL 100C electron microscope fitted with an objective lens of $C_s = 0{\cdot}67$ mm. The specimen was not tilted relative to the incident beam. Images at a magnification of 17 000 × were recorded on X-ray film – Ilford G – and the technique of minimum exposure was employed as described in detail previously (Fryer, 1978), approximately five seconds exposure to the electron beam causing complete specimen destruction.

Measurements made on molecular images relied upon an accurate calibration of the electron microscope. This was done by obtaining lattice images of graphite (3·4 Å), chrysotile asbestos (7·3 Å) and chlorinated copper phthalocyanine (26 Å) in the magnification range used for this work. Another source of error lay in the subsequent enlargement of the micrograph. Care was taken to minimize this so that the errors on the unit-cell parameters measured were less than 2% in absolute values whilst the ratios of unit-cell distances, measured from the same micrograph, were less than 1%. Selected-area diffraction measurements have associated errors of 2% when compared with a standard material but again ratio measurements on the same diffraction pattern are of higher accuracy.

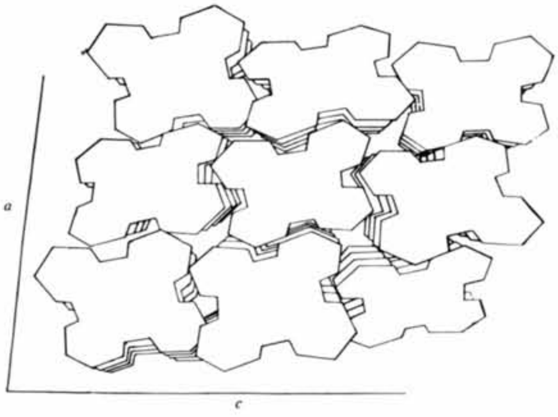

Fig. 2. Molecular columns of phthalocyanine showing how imaging parallel to the *b* axis would give the *ac* projection.

## Results and discussion

### 1. *Film structure*

The evaporated films of phthalocyanine were in the form of discrete islands, as shown in Fig. 3, indicating that some annealing had taken place during preparation at 493 K. The islands were aligned in similar directions such that electron patterns characteristic of a single crystal were obtained.

Experiments with chlorinated copper phthalocyanine and platinum phthalocyanine have shown that, even after annealing, the molecules lie flat on the substrate with the result that the axis of a column of superimposed molecules is inclined at an acute angle to the substrate – the complementary angle to that made to the *b* axis by the molecular plane. Consequently, molecular images cannot be obtained without tilting the specimen as described previously (Murata, Fryer & Baird, 1976*b*). In both of these phthalocyanine derivatives the angle subtended by the molecular plane to the column axis was 60°, thus requiring a tilt of 30° for imaging, whereas in phthalocyanine it is 45° 48′.

In this preparation of phthalocyanine on KCl the molecules did not align parallel to the substrate and the column axis was normal to the substrate. Therefore specimen tilting was not necessary. It appears probable that a critical molecular angle exists, beyond which the advantages of a parallel superimposition of the molecules are outweighed by the strain incurred in having a sharply inclined column axis. For phthalo-

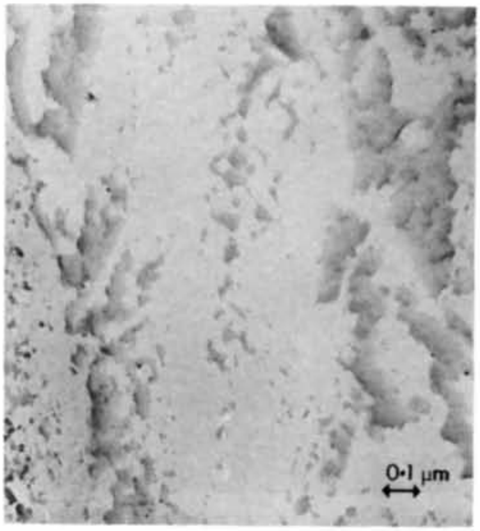

Fig. 3. Evaporated film of phthalocyanine.

cyanines this angle would lie in the range 30–40°. In the phases and transformations observed there was no tendency for the molecular column axis to deviate from being normal to the substrate as illustrated in Fig. 2. For phthalocyanine it is clearly a stable orientation.

## 2. *Unit-cell parameters*

The molecular column axis was parallel to the incident beam so that the molecular images shown in Fig. 4 represent the *ac* projection. The diffraction pattern is illustrated in the insert. The lattice constants, based on a $C2/c$ unit cell, are $a = 26$, $c = 25{\cdot}4$ Å, $\beta = 91°$ from the micrograph and $a = 25{\cdot}6$, $c = 24{\cdot}8$ Å, $\beta = 91°$ from the diffraction pattern. The $b$ axis cannot be determined in this orientation. The diffraction values might be expected to be more accurate since they are the average of many more unit cells than in the micrograph, but both sets of data give an $a/c$ ratio of 1·03. The data reported by Ashida, Uyeda & Suito (1966) for phthalocyanine prepared on muscovite gave an $a/c$ ratio of 1·10. Thus the present data are at variance with Ashida's values as well as the bulk values reported by Robertson (1935) and Donnay & Donnay (1963). It can therefore be concluded that for phthalocyanine the lattice constants of epitaxic thin films are influenced by the substrate on which they have been prepared. This is probably a more satisfactory conclusion than postulating a plethora of polymorphs.

Such deviations of lattice parameters have not been observed in metal phthalocyanines and it is possible that there is some lability of the hydrogen atoms attached to the pyrrole nitrogen atoms causing a charge on the nitrogen that would affect the whole molecule. A charged molecule would be considerably influenced by the coulombic forces pertaining in the KCl substrate, these forces being much more powerful and of longer range than van der Waals dipolar interactions. The comparative ease of formation of such charged molecules is suggested by the changes in dielectric constant observed by Vidadi, Chistyakov & Rosenshtein (1969).

Another crystalline phase observed is shown in Fig. 5. In this micrograph the molecules are in white contrast. The occurrence of this phase was much less widespread than that shown in Fig. 4 and it has lattice constants of $a = 27{\cdot}8$, $c = 23{\cdot}8$ Å and $\beta = 116°$, again for a $C2/c$ space group assuming the non-determinable parameters are in agreement. The crystals were small and usually situated in close proximity to the other phase so that a clear diffraction pattern could not be obtained. The unit cell of this phase is delineated in Fig. 5 and the parameters do not resemble any previous measurements. This phase is clearly a distinct polymorph and may represent an intermediate between the low-temperature form that is produced below 473 K and the high-temperature form that is produced at 673 K. Susich (1950) has reported three polymorphs and it is possible that the formation temperature in this work, 493 K, just permitted a higher-temperature polymorph to form. In all cases the polymorph was influenced by the presence of the substrate.

## 3. *Phase transformations*

The structural relationship between the two phases is illustrated by Fig. 6. Again the molecules are in white

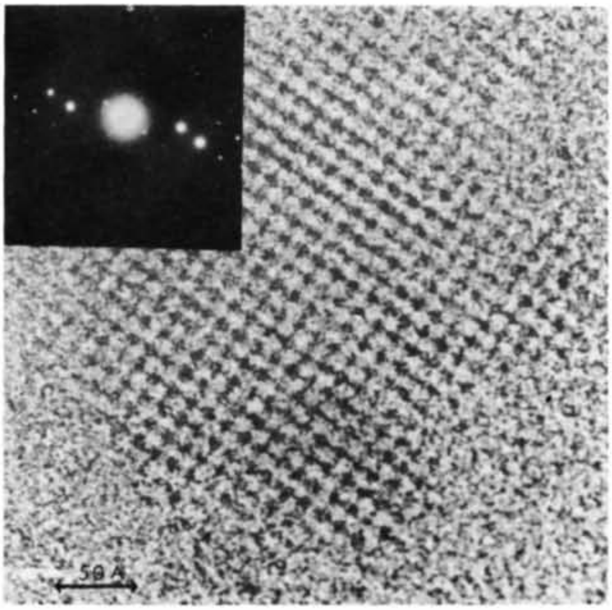

Fig. 4. Molecular image of a polymorph of phthalocyanine, molecules in black contrast. Phase *A*. Inset: diffraction pattern.

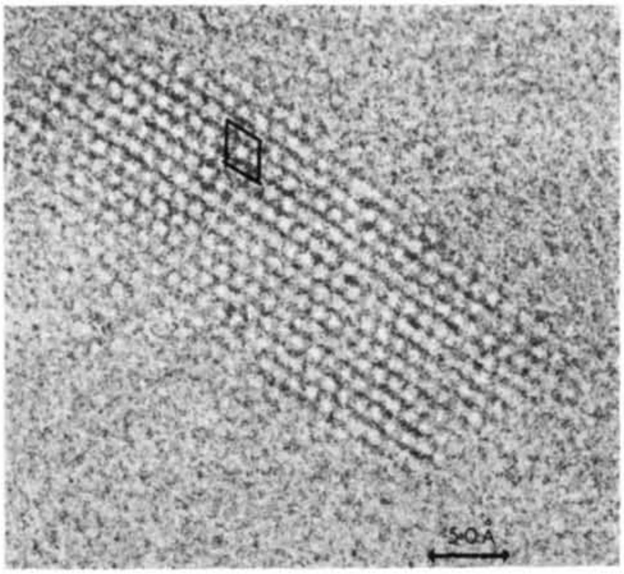

Fig. 5. Molecular image of another polymorph of phthalocyanine, the molecules in white contrast. Phase *B*.

contrast but the two phases are clearly defined with a common boundary in their (100) planes marked *CD*. For definition the approximately orthorhombic phase is termed *A* and the other phase is termed *B* as marked in Fig. 6.

The optical diffraction patterns of the two phases and the phase boundary are shown above in Fig. 6, showing that the change occurs by alteration of the unit-cell angle with only minor adjustments to take up the different unit-cell distances.

The transformation fulfils the conditions for a martensitic phase change as far as can be judged from the two-dimensional image. There is a sharp boundary with a common lattice plane accompanied by a change in the crystal shape. Such a transformation is substantiated by the lamella marked *EF* in Fig. 7 and by the lamella running down the crystal in Fig. 5. In both phases the columns of molecules remain parallel to the incident beam so that there is no component across the phase boundary.

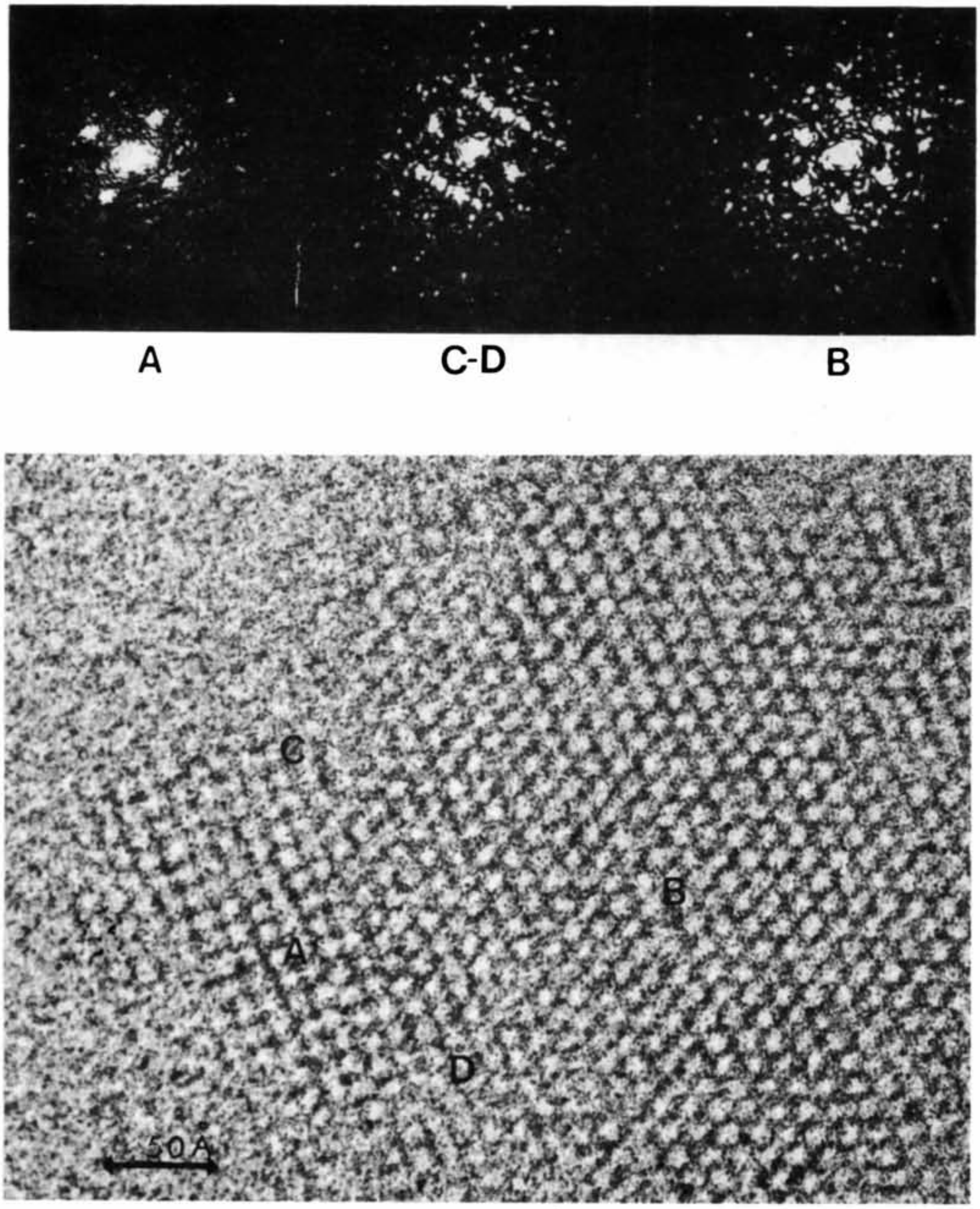

Fig. 6. Phase transformation between polymorphs of phthalocyanine. The phase boundary is marked *CD*. The optical diffraction patterns of the two phases and the phase boundary are shown above. The molecules are in white contrast.

The two phases are apparently of similar energies since they readily convert to each other given a slight stimulus. In consequence distortions are easily accommodated, provided the columns of molecules retain their integrity and normality to the substrate. Such distortion is seen in Fig. 6 in phase *A*. This distortion may have been caused by the proximity of the phase boundary, and the confinement of the distortion to this phase substantiates the proposal that phase *A* is of lower stability than phase *B* – *i.e.* it is the lower temperature phase. The lamellae do not show such distortion, however, but the symmetrical environment either side of the lamellae may serve to cancel out distortion.

The lattice energies and surface energies of molecular crystals are usually small and this appears to be the case for phthalocyanine. Even small crystals of five molecules diameter retained their crystallographic identity with no distortion of the interplanar spacings at the periphery of the crystals. This may be indicative of the absence of long-range forces but on plane faces and corners, individual columns of molecules remained in perfect crystallographic positions. Under longer irradiation from the electron beam the corners became rounded but this was caused by thermal ablation rather than surface rearrangement. It is of interest that isolated columns of molecules on plane faces retain such crystallographic perfection. The quadrilateral column would only have contact with the crystal on one side, indicating that the attractive forces are significant and possibly are augmented by some electron flow as shown by the semiconductor properties of this material. The short-range attractive forces, however, must be dominant otherwise there would be a significant difference between large and small crystals.

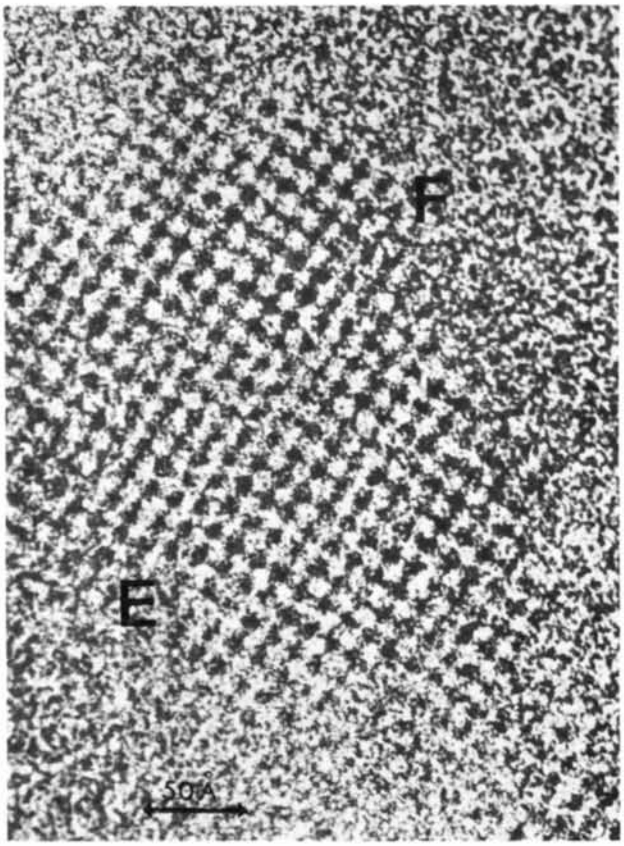

Fig. 7. Phase *A* phthalocyanine containing a lamella of phase *B*, marked *EF*.

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