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Transmission electron microscopic observation of dislocations in x-phthalocyanine crystals

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Transmission electron microscopy has been utilized to directly reveal the defects that are present in thin single crystals of x-phthalocyanine polymorph. The bright field images are characteristic of dislocation arrays while the associated diffraction patterns indicate that the parent monoclinic structure of x-phthalocyanine may undergo a stress-induced phase transformation into a daughter orthorhombic structure. The transformation is akin to a martensitic process as a result of the operation of an invariant plane strain. The dislocation arrays observed have been interpreted in terms of slip dislocations.

1. Introduction

Among the five known phthalocyanine polymorphic crystals that have been extensively studied for their semiconducting, photoconducting and dielectric properties, the x-polymorph exhibits superior photoconductivity and charge acceptance [1–3]. In the present paper we report on transmission electron microscopic observations of dislocations present in x-phthalocyanine crystals. The dislocations in phthalocyanines are of interest from a fundamental point of view; it is of interest to determine what types of dislocations exist in this organic crystal and how they compare with dislocations observed in other organic crystals. It is also desirable to learn if there is any correlation between the presence of dislocations, their type and number, and the photoconductivity of phthalocyanines. Susceptibility to electron beam damage is at present a key factor limiting the information obtainable from electron microscopic studies of these crystals, though the usual precautions to minimize the radiation damage of the sample have been taken during observation [4, 5].

2. Materials and methods

Fig. 1 is a typical electron micrograph of x-phthalocyanine crystals. The crystals have a lath morphology (3 to 5 μm long and about 0.5 μm wide) and besides a number of bend extinction contours, there is an array of parallel lines, about 25 to 35 nm apart running parallel to the short crystal axis. The linear contrast has been interpreted as due to dislocation arrays.

The usual method employed in analysis of dislocations, i.e. the $\boldsymbol{gb}$ invisibility criterion [6], was difficult to carry out because of many similar interplanar spacings and because of pronounced bending of the crystals which led to multiple beam conditions. In addition, the x-phthalocyanine crystals exhibited only $\langle 001 \rangle$ orientation yielding diffraction information from only $(hk0)$ planes; nothing could be learnt about the c-axis component.

In order to deduce the nature of the dislocation images obtained under such limiting experimental diffraction conditions, theoretical considerations of possible Burgers vectors of dislocations were derived from an analysis of the crystal structure, and combined with the available experimental data.

3. Results and discussion

As a result of X-ray analysis carried out on x-phthalocyanine crystals in this laboratory, a monoclinic crystal with lattice parameters $a = 2.386$ nm, $b = 0.493$ nm, $c = 0.994$ nm and $\beta = 98.4°$ has been proposed, and is schematically represented in Fig. 2. The shortest lattice translation vectors are marked. The commonly excited $\boldsymbol{g}$ (operating reflection) was (200) and hence the $\boldsymbol{gb}$ visibility condition would be satisfied for dislocations having Burgers vectors of values $\langle \frac{1}{2}00 \rangle$. Also, Burgers vectors of values $\langle 120 \rangle$, $\langle 102 \rangle$, $\langle 101 \rangle$ and $\langle 111 \rangle$ would satisfy a visibility criterion of higher value ($\boldsymbol{gb} = 2$) but these double line dislocation images have not been observed. Some electron micrographs show contrast similar to Moiré fringes due to high extinction distances (more than 100 nm) as compared to the distances between the dislocations in the array [7], though there are examples where the dislocation arrays have been made distinct by slightly changing the diffraction condition in order to reduce the strain contrast, as demonstrated by Figs 3a and b.

The associated diffraction pattern of the faulted region of x-phthalocyanine (insert in Fig. 1a), as indexed in the tracing in Fig. 1b, shows the $\langle 001 \rangle$ projection of the monoclinic crystal structure, with $(hk0)$ rows excited. However, half-way between the spots of the $(hk0)$ rows there are extra diffraction spots, which could neither be accounted for by double diffraction nor by twinning of the original monoclinic crystal. On the other hand, the diffraction pattern of the unfaulted region (free of dislocation arrays) of x-phthalocyanine crystals, presented in Fig. 4a which, with its corresponding tracing in Fig. 4b shows again

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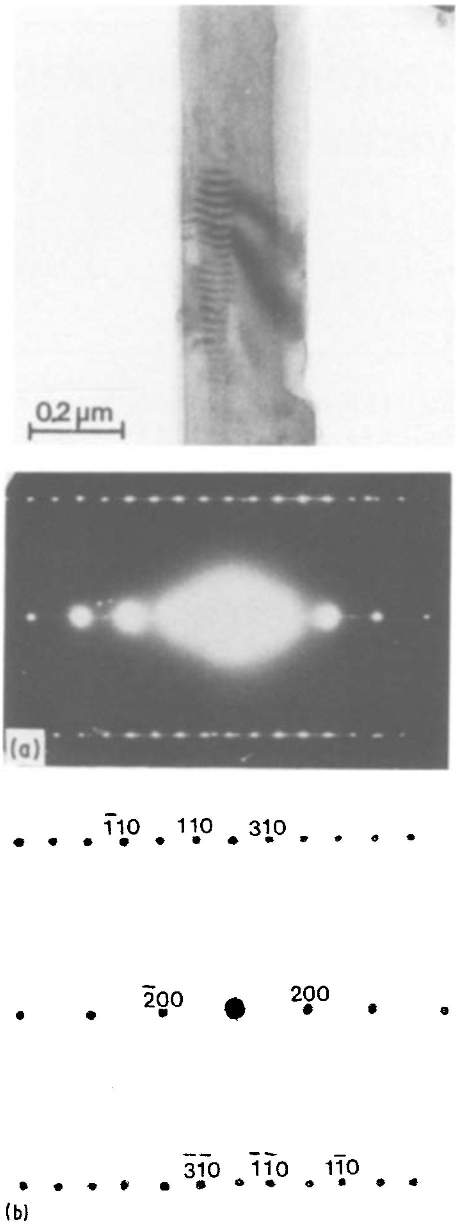


Figure 1 (a) Transmission electron micrograph of dislocation arrays in x-phthalocyanine crystal with the associated diffraction pattern. (b) Tracing of the diffraction pattern of (a).

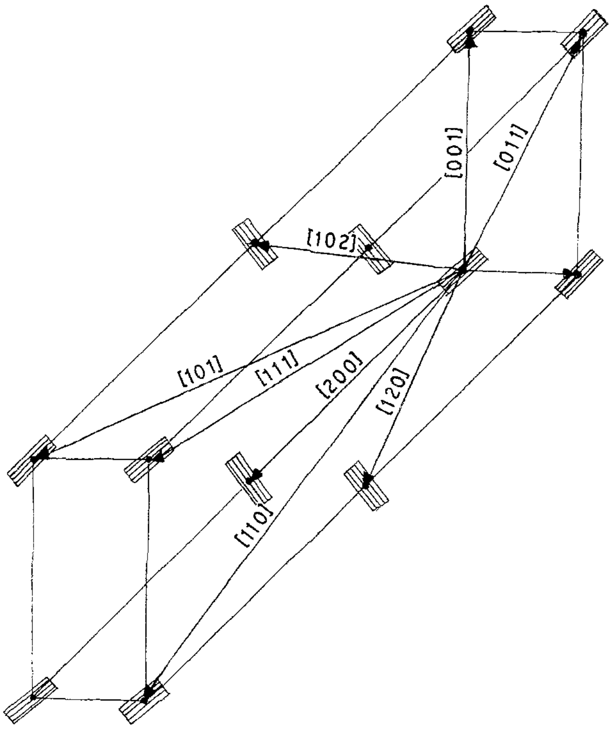


Figure 2 Schematic representation of the crystal lattice of x-phthalocyanine crystal.

the $\langle 0\,0\,1 \rangle$ projection of the monoclinic crystal structure without the extra diffraction spots existing on $(h\,k\,0)$ rows. Figs 5a and b are two more examples of faulted regions of x-phthalocyanine crystals emphasizing further the commonly observed feature of dislocation arrays with associated diffraction pattern consisting of extra spots in $(h\,k\,0)$ rows of the monoclinic crystal lattice.

The presence of extra diffraction spots in the diffraction patterns of faulted regions of x-phthalocyanines has been interpreted as due to the presence of an orthorhombic crystal cell with lattice parameters a and b as for the monoclinic x-phthalocyanine but with a different c parameter. The two-dimensional unit cell of the proposed orthorhombic crystal lattice is schematically drawn in Fig. 6, superimposed on the parent, monoclinic lattice diffraction pattern.

The presence of an orthorhombic crystal structure in the x-phthalocyanine having monoclinic crystal structure, suggests that the parent monoclinic structure of x-phthalocyanine has undergone a phase transformation into a daughter orthorhombic structure. A phase transformation in which an orthorhombic lattice shears into a monoclinic one is characteristic of martensitic modes of phase transformations and is known to exist in single crystals of polyethylene [8–11] and 1,8-dichloro-10-methylanthracene [12].

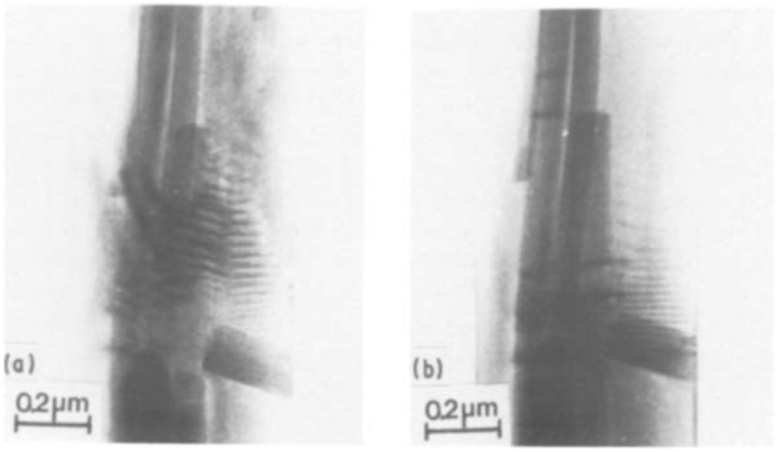
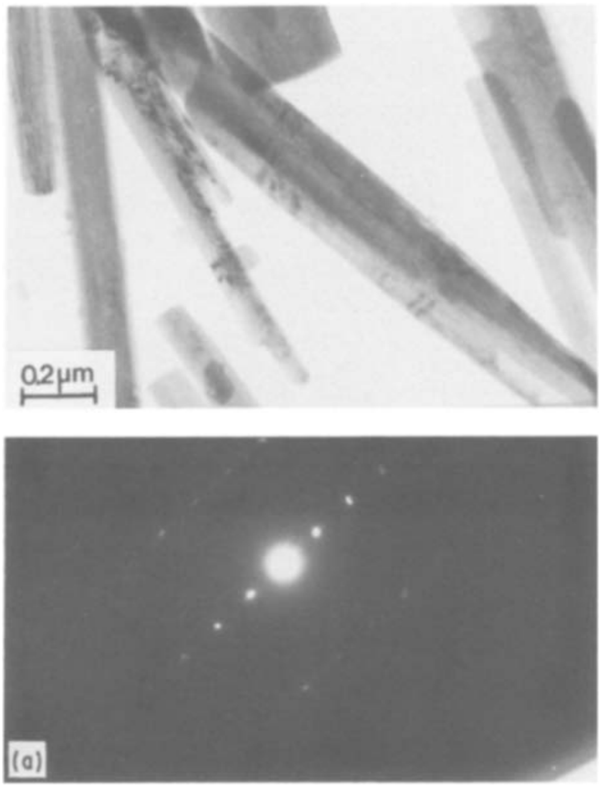


Figure 3 (a) and (b) Transmission electron micrographs of a dislocation array at different tilt angles.



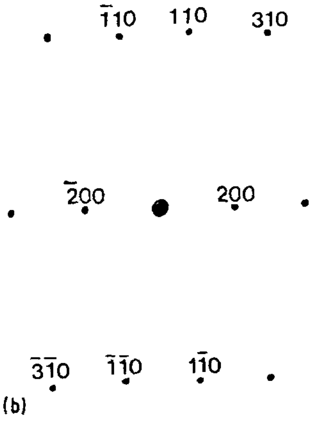


Figure 4 (a) Transmission electron micrograph of unfaulted region of x-phthalocyanine crystal with the associated diffraction pattern. (b) Tracing of the diffraction pattern of 4(a).

Fig. 7a is a drawing representing the shear elements involved in the proposed monoclinic to orthorhombic phase transformation in x-phthalocyanine crystals. With the available experimental data it was not possible to assign a unique shear mode of the transformation but the diffraction pattern data indicate that the lattice correspondence is $\langle 1\,0\,0\rangle_m \parallel \langle 1\,0\,0\rangle_o$ and $\langle 0\,1\,0\rangle_m \parallel \langle 0\,1\,0\rangle_o$, which would agree with $\bar{1}3_2$ mode of an orthorhombic to monoclinic martensitic transformation as given in the studies of Bevis and Crellin [8, 9], and is schematically represented in Fig. 7b.

In the light of the above discussion, the dislocation arrays observed in x-phthalocyanine crystals have been interpreted as slip dislocations which are responsible for the shearing of the monoclinic crystal lattice. From the contrast experiments, the visibility conditions of dislocation images were obtained with the operating reflection $g(2\,0\,0)$ suggesting the Burgers vectors $\langle \frac{1}{2}0\,0\rangle$ and (a plausible) slip system $(0\,1\,0)\langle \frac{1}{2}0\,0\rangle$ operative.

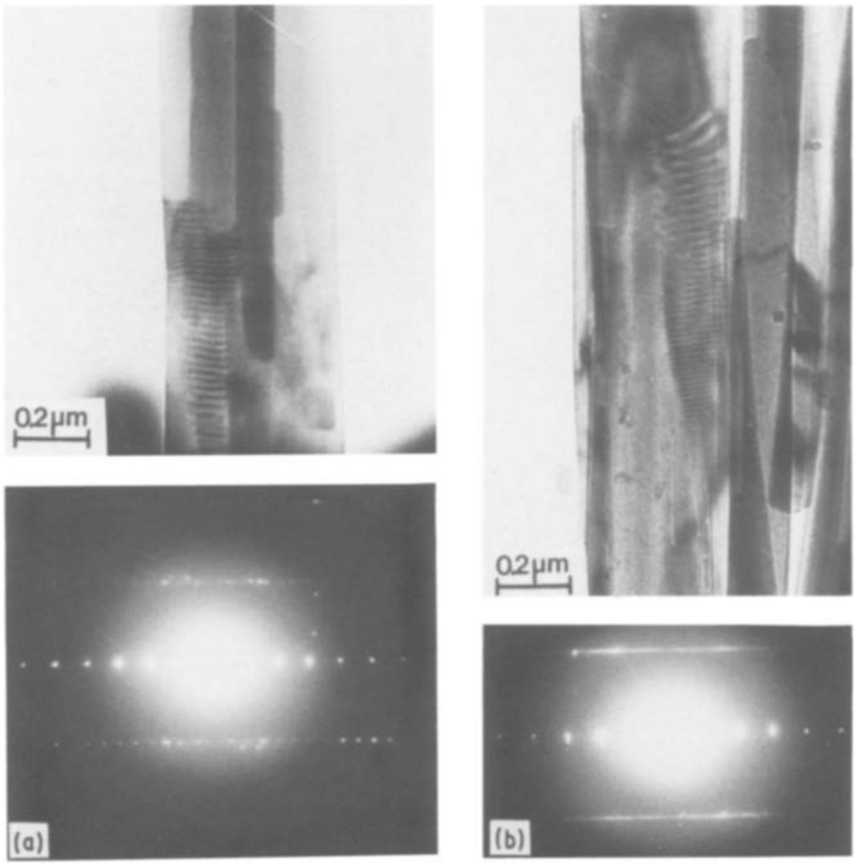


Figure 5 (a) and (b) Transmission electron micrographs of faulted x-phthalocyanine crystals with the associated diffraction patterns.

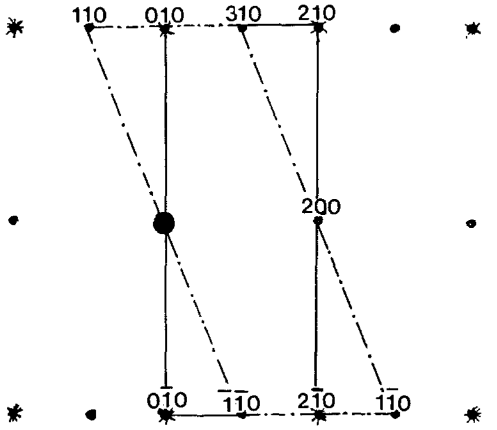


Figure 6 Schematic representation of the two-dimensional unit cell proposed for orthorhombic crystal lattice (∗) superimposed on the parent monoclinic crystal lattice (·).

The proposed monoclinic to orthorhombic martensitic transformation might occur during x-phthalocyanine formation in the process of neat-milling. The collisions of x-phthalocyanine particles with steel beads during neat-milling may cause a small stress, yet large enough to shear the monoclinic crystal lattice into an orthorhombic one, or to nucleate a spontaneous martensitic transformation.

4. Conclusion

The bright-field transmission electron microscopy of x-phthalocyanine crystals has revealed images characteristic of dislocation arrays, while the associated diffraction patterns indicate the presence of an orthorhombic crystal structure, suggesting the stress-induced phase transformation of the monoclinic to an orthorhombic crystal structure, akin to a martensitic mode of transformation. The new orthorhombic unit cell and the martensitic reaction mode are conjectured, on the basis of limited experimental evidence. The observed dislocation images have been further interpreted as slip dislocations, which are responsible for the shearing of the monoclinic into the orthorhombic crystal structure.

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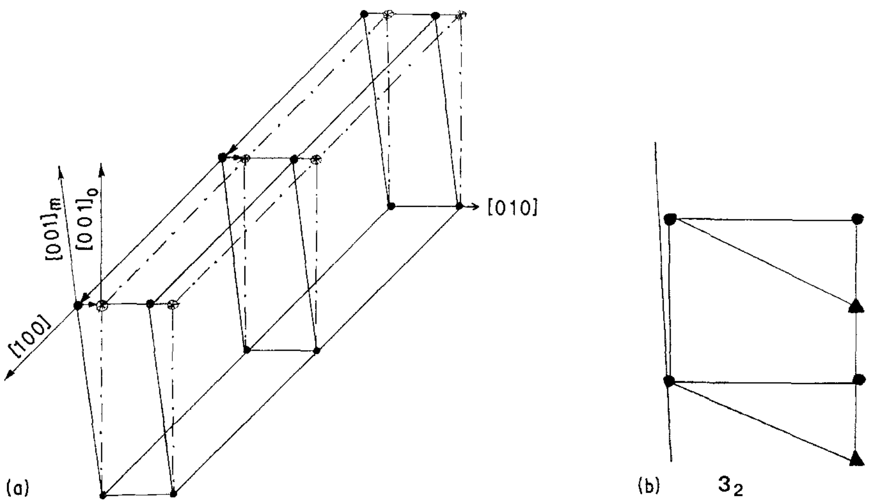

Figure 7 (a) Schematic representation of the shear mode involved in the proposed monoclinic–orthorhombic phase transformation in x-phthalocyanine crystals. (b) Schematic representation of the (0 0 1) plane of shear plot for orthorhombic–monoclinic $\bar{1}3_2$ mode martensitic transformation as given by Hay and Keller [11].