Direct observations of polytypism in copper phthalocyanine

D. G. HOWITT
Department of Mechanical Engineering, University of California, Davis, CA 95616, USA

Extended regions of alternative molecular packing have been identified in single crystals of β-copper phthalocyanine by transmission electron microscopy. The interface separating the regions of transformed crystal are structurally equivalent to an array of partial dislocations on alternate (0 0 1) planes of the β-phase which can be seen to migrate under the influence of the microscopes' electron beam. The energy difference between the two planes was approximately 0.1 kJ mol^{-1} at room temperature, considerably smaller than the value reported to be the difference between the α and β phases.

1. Introduction

There is a great deal of evidence to suggest that the electrical and chemical properties of crystalline organic materials can be modified, if not governed, by defects which disturb the prevailing orientation of the constituent molecules [1, 2]. Partial dislocations have been directly inferred to govern the course and stereochemical products of a number of photochemical reactions displayed by anthracene and some of its derivatives [3, 4]. Although dislocations and phase separation have been observed directly by electron microscopy in these materials, boundaries separating these structures have not been identified.

The direct confirmation of defects by electron microscopy is far from straightforward in organic materials because of the severity of the radiation damage which is induced by the electron beam. In consequence, much of the electron microscopy has been confined to diffraction contrast techniques where the electron dose required to record an image is substantially smaller than that for the alternative high resolution methods. In the more radiation resistant materials such as copper phthalocyanine high resolution lattice imaging can be used to advantage and in this way the stress induced β → α transition which occurs in this material was detected [5]. The mechanism of the transformation was thought likely to be a shear type although the orientation relationships with the matrix could not be identified.

In this investigation high resolution electron microscopy has been used to examine the structure of copper phthalocyanine outside the orientations suitable for molecular imaging. The molecules are therefore imaged in an end-on rather than a facing orientation which is more appropriate for studying differences in their stacking sequences (Fig. 1).

2. Experimental details

Single crystals of copper phthalocyanine suitable for examination by transmission electron microscope (TEM) were prepared from commercially available powders grown by sublimation. The powders were separated ultrasonically and subsequently suspended in ethanol. The suspension was deposited onto formvar coated grids by dropwise evaporation to produce specimens in the shape of long, thin ribbons approximately 500 Å thick.

β-copper phthalocyanine is one of the more radiation resistant organic materials known and although it is a thousand times more resistant than amino acids [6], an exposure to the conventional electron beam currents used in high resolution electron microscopy will destroy it in seconds. Although decreasing the electron dose rate can postpone the destruction of the specimen, to outlast the time periods of experimental operation, the significance of any result is ultimately determined by the total electron dose used and the effect this dose has on the specimen. In order to minimize the electron dose to record micrographs,
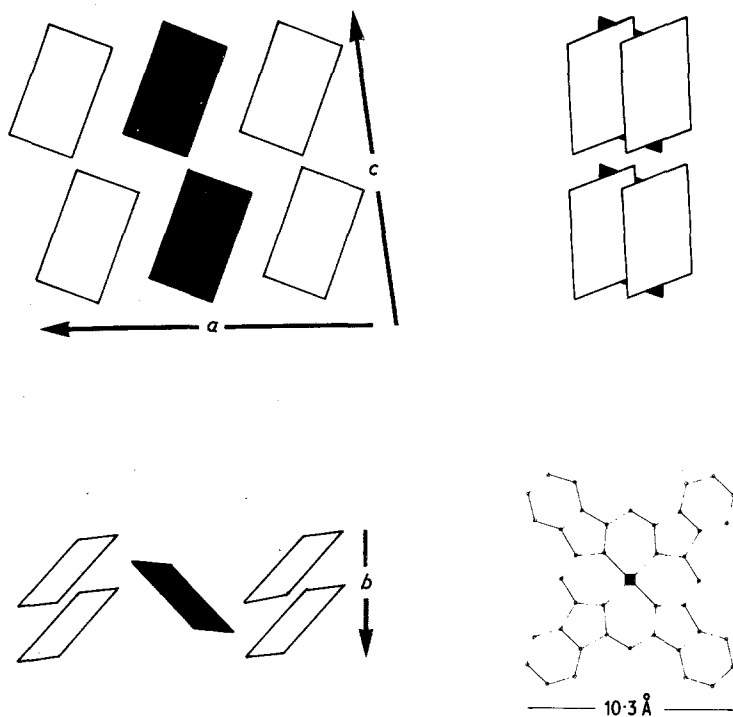
Figure 1 The crystal structure of β-copper phthalocyanine. The molecules are depicted as projected squares and the difference in shading indicates a dissimilarity in orientation.

Kodak no-screen X-ray film was substituted for the conventional electron image plates. This film, although of poorer resolution, more efficiently records electrons in an overall comparison. To obtain the maximum advantage from the efficiency of this film, recordings were made at image magnifications where the expected image resolution and ultimate film resolution were comparable; the image magnification corresponded to 50 000 times for a resolution of 4 Å.

The electron microscope used was a Siemens Elmiskop 102 ($C_s = 2.9$ mm). The most convenient exposure time for image recordings was about 20 sec which represented a reasonable compromise between the mechanical stability of the microscope and the periods of experimental procedure. To preserve the mechanical stability of the specimen, constant electron beam currents of about 0.15 Ccm^{-2} were used. In copper phthalocyanine it was found that ten micrographs with optical densities of unity could be recorded before all traces of crystalline structure were lost in diffraction. The high resolution images of copper phthalocyanine were all recorded from symmetrical orientated diffraction patterns with the transmitted beam aligned to the optic axis of the microscope. The defocus was estimated to be about 500 Å and was based upon the distinguishability at these low levels of illumination of bright fresnel fringes at approximately 1000 Å defocus around the holes in the formvar film. The critical exposure of copper phthalocyanine was found to be too short to permit through focus series to be recorded in which the individual micrographs are still representative. To maximize contrast, the size of the objective aperture was chosen to exclude detail finer than the photographic film could record and the image resolution was determined using techniques of optical diffraction with a helium—neon laser.

3. Results

Analysis of the copper phthalocyanine specimens by electron diffraction showed the presence of two distinct phases; the established β-form and a second phase which as far as could be determined differed from it only by the presence of additional diffraction spots which correspond to a doubling of the interplanar spacing of (0 0 1). Whilst other crystalline forms of copper phthalocyanine have been identified [7, 8], the second phase identified here has not previously been reported.

The correspondence of all the diffraction spots of the β-phase to those of the second phase were, as far as could be determined by electron diffraction, exact and this spacing did not correspond to any fundamental reflection of the β-phase.

The microstructure of the two-phase structure

1250
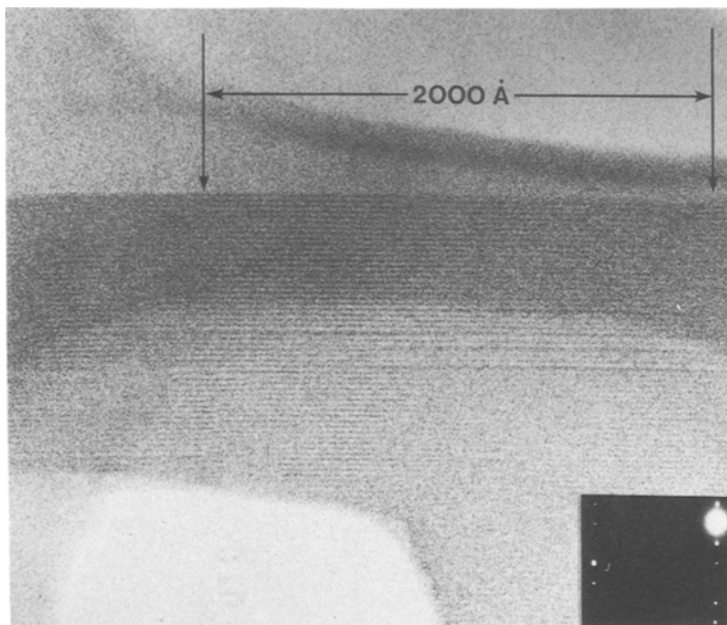
Figure 2 A region of two-phase structure in a copper phthalocyanine crystal and selected area diffraction from the region. The diffraction pattern exhibits the additional reflections derived from the second phase.

is best revealed by simultaneously lattice imaging the $(0\,0\,l)$ type reflections from both phases (Fig. 2). This microstructure was on too fine a scale to isolate the regions of second phase by selected area diffraction and it was only in the image mode that the presence of a two-phase structure could be detected. The critical exposure, which was the electron dose to destroy crystalline diffraction, was the same for both phases $(3\,\mathrm{Ccm}^{-2})$.

Although the fine distinction in structure did not effect the end point of radiation damage, the manner in which the two phases responded was quite different. In diffraction, whilst the β-phase was dominated by the loss of high resolution detail, the other phase lost, in addition, the lowest order $(0\,0\,l)$ reflections after an electron dose equivalent to about one-third of the critical exposure. This ultimately left a diffraction pattern which was indistinguishable from that of the β-form.

The very early effects of irradiation, which occurred before the apparent loss of the second phase, could be monitored in the lattice images. In Fig. 3 four successive micrographs showing this degradation at intervals of $0.1\,\mathrm{Ccm}^{-2}$ are shown. The first stage is the transformation of the region of β-phase, which originally extended to a width of 1900 Å. This was completed within an electron dose of $0.5\,\mathrm{Ccm}^{-2}$. It is for this reason that the faint contrast from the broad-banded faults within the second-phase extended into the region of β-phase in the earliest micrograph; the separating interfaces were moving during the electron exposure necessary for the recording $(0.2\,\mathrm{Ccm}^{-2})$. These broad bands are present in both the adjacent regions of second-phase, they are not continuous but merely adopt similar positions laterally within the host crystal. The annihilation of the β-phase was not reversed with continued electron exposure, however, the contrast from the additional reflections within the second-phase was lost to lattice images corresponding to exactly half this spacing after an electron dose of $1.0\,\mathrm{Ccm}^{-2}$. The loss of contrast in this way is more clearly shown in Fig. 4.

4. Discussion

In complex structures such as copper phthalocyanine (Fig. 1), where large molecules of limited symmetry occupy the lattice sites, the interplanar spacings within the crystal are governed by the orientation relationships which exist between the adjacent molecules.

The exact correspondence between reflections of the $\{h\,k\,0\}$ type in the two phases observed here indicates that the molecular configuration which comprises the $(0\,0\,1)_\beta$ planes is common to both structures. The distinction between the two phases can also be definitively interpreted in terms of an alternative stacking of these planes, rather than a compositional ordering of the molecules. This is
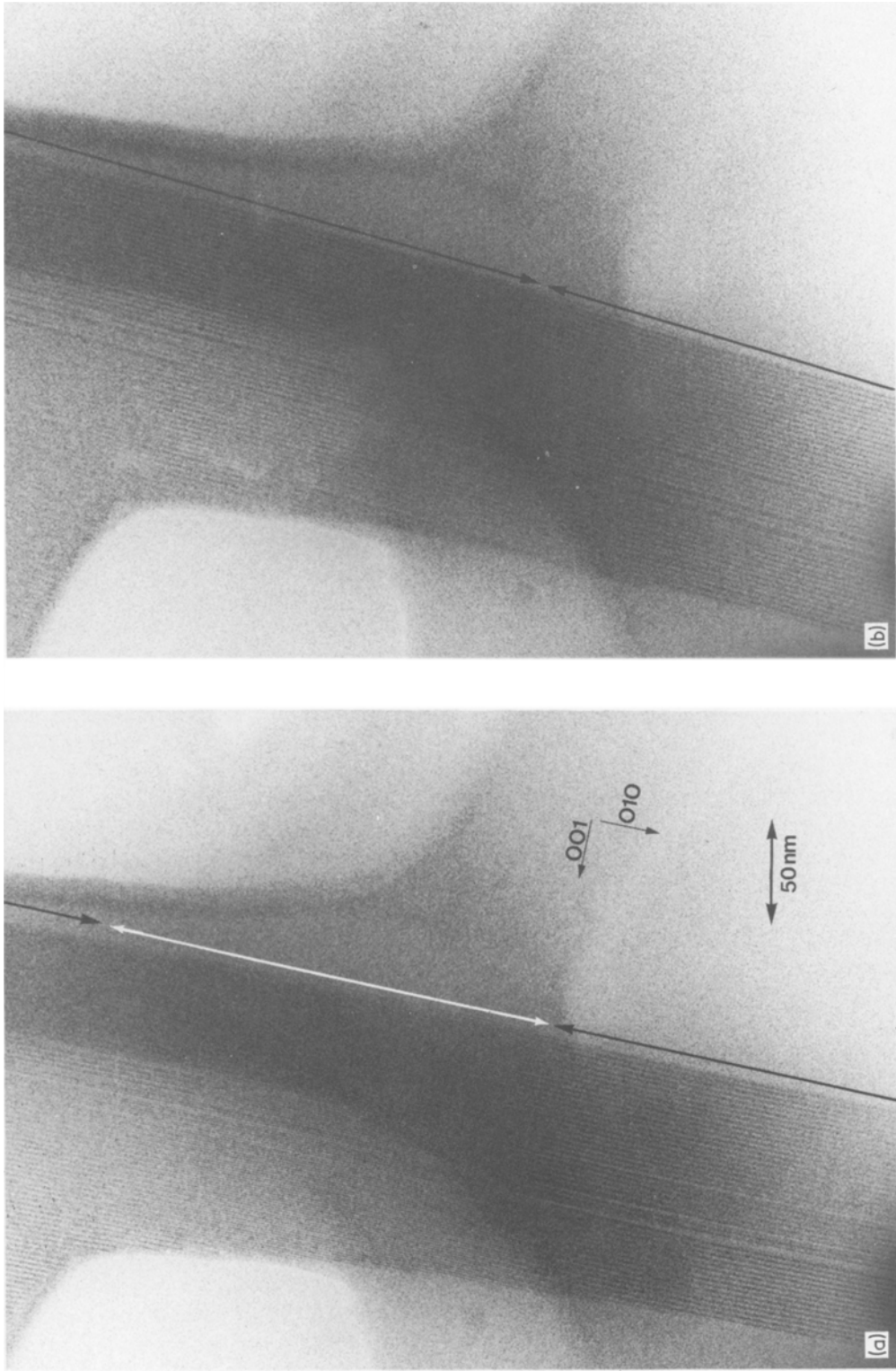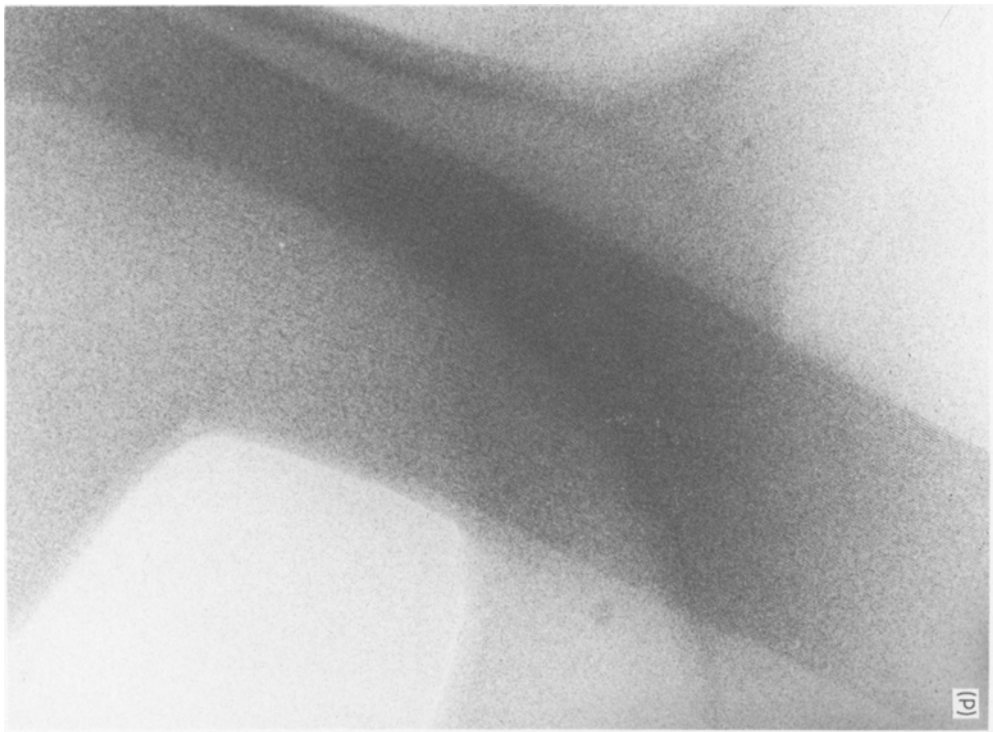
Figure 3 The effects of radiation damage to the two-phase structure of copper phthalocyanine after electron doses of (a) $0.2\,C\,cm^{-2}$ (b) $0.5\,C\,cm^{-2}$ (c) $0.8\,C\,cm^{-2}$ and (d) $1.1\,C\,cm^{-2}$.

Figure 3 Continued.

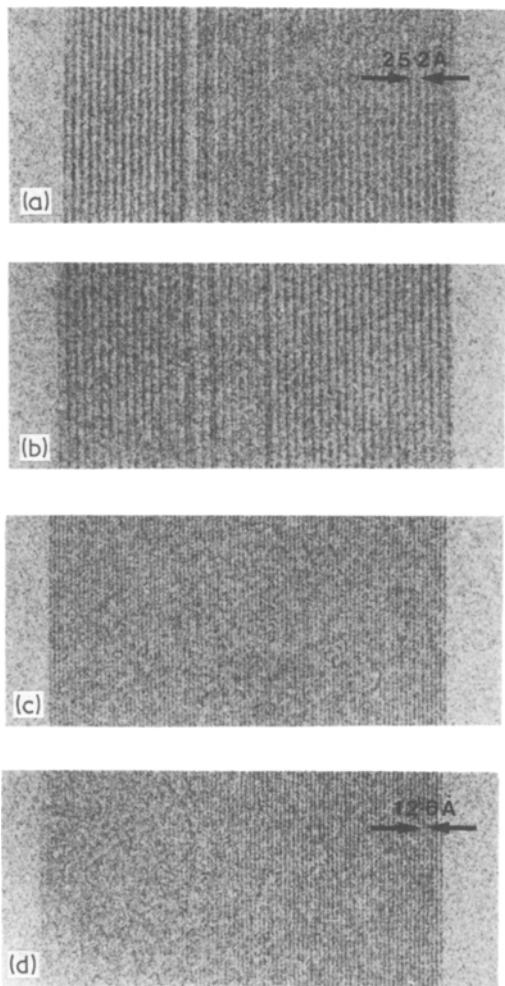*Figure 4* The effects of radiation damage to the second phase of copper phthalocyanine. The electron doses are (a) $0.2\,Ccm^{-2}$ (b) $0.5\,Ccm^{-2}$ (c) $0.8\,Ccm^{-2}$ and (d) $1.1\,Ccm^{-2}$.

because the loss of the additional reflections from the second phase has to be brought about by ionization processes and these effects are not associated with long-range atom transport in organic materials [6]. The severity of the ionization processes precluded the complete determination of the boundary structure before it disappeared. Nevertheless, the structure of the second phase and the interfaces are not completely arbitrary since no superlattice reflections other than the $(0\,0\,l)$ type were observed. In order to maintain the absence of these reflections, the stacking of the $(0\,0\,1)_\beta$ planes can only have been changed in one of two ways. A displacement could have been introduced between them of either

$[1/2, 0, 0]$ or $[0, 1/2, 0]$. The first would produce the type of misorientation suggested by Thomas [9], where the dislocation is a partial dislocation. The second would produce a misorientation via a defect akin to the leading half of a superdislocation found in ordered metallic alloys [10].

It is important to note that the variations in the molecular symmetry brought about by either of these changes do not in themselves introduce any additional diffraction spots. The reflections of the second-phase are brought about by the lattice displacements involved in the accommodation of the different near neighbour configurations at the stacking fault. The additional reflections are therefore due to two alternate interplanar spacings which have the period of their sum. This is readily apparent from a consideration of the kinematical structure factor for the second phase given by

$$F_{\mathbf{g}} = \sum_{\text{unit cell}} \left\{ \sum_i f_i(\theta) \exp 2\pi i \, (\mathbf{g} \cdot \mathbf{r}_i) + \right.$$

$$\left. + \sum_j f_j(\theta) \exp 2\pi i \, (\mathbf{g} \cdot \mathbf{r}_j) \right. \tag{1}$$

where $f_n(\theta)$ is the appropriate atomic scattering factor for the atom at r_n in the unit cell and i and j refer to the molecules of different orientation where

$$\mathbf{r}_j = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \mathbf{r}_i. \tag{2}$$

The reflections of the type $\mathbf{g} = 0\,k\,l$ have a structure factor

$$F_{\mathbf{g}} = 2 \sum_{\text{unit cell}} \sum_i F_i(\theta) \exp\left(2\pi i \left[(k + l) \cdot r_i\right]\right). \tag{3}$$

In the case of the introduction of either of the stacking modifications discussed this structure factor is unchanged. The additional reflections are introduced only when a change in the molecular orientation results in a change in the near neighbour spacing and hence a direct change in the dimensions of the unit cell (Fig. 5).

The mobility of the interfaces separating the phases under radiation damage and the expansion of the second-phase at the expense of the stable β-phase suggests that the microstructure could be appropriately interpreted in terms of a dislocation model where an array of dislocations, derived from split dislocations on every other $(0\,0\,1)$ plane,
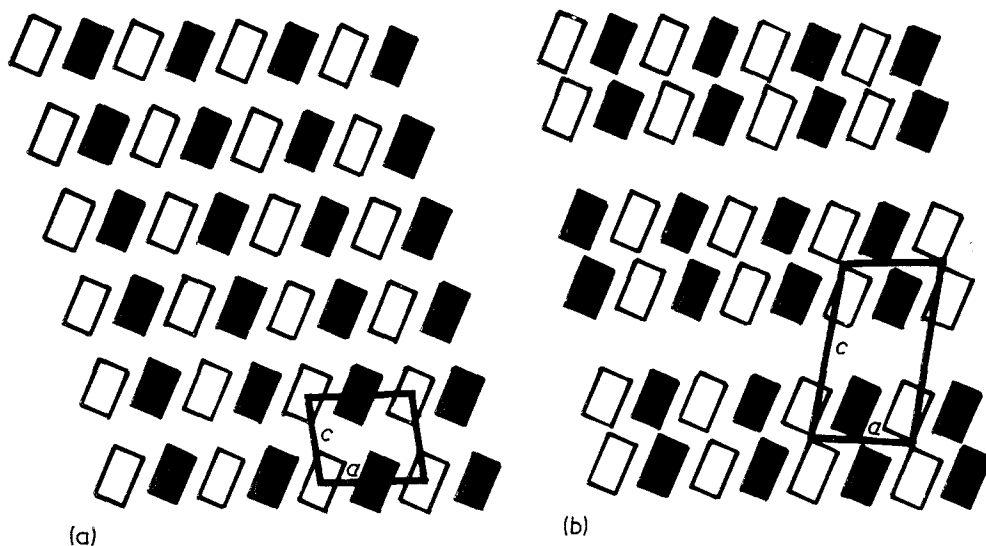
Figure 5 [1 0 0] projections of the molecular structure of (a) the β-phase of copper phthalocyanine and (b) the additional phase identified here.

bounds the transformed phase. The distance separating the partial dislocations on every plane would be characteristic of a stacking fault energy. This, to a large extent, has to be dependent upon the distortions which are introduced in the accommodation of disoriented molecules. The destruction of the molecules by radiation damage would reduce the magnitude of the stacking fault energy by alleviating this distortion, inducing a larger separation of the bounding partial dislocations on each plane. This increase in separation would correspond to the transformation of the β-phase by the migration of the interfaces under radiation damage.

The motion of these interfaces (Fig. 3) show that if this is the mechanism, then at least a substantial component of the Burgers vectors of the partial dislocation must lie along $[0\,1\,0]_\beta$. In β-copper phthalocyanine this is the shortest lattice vector (4.79 Å), and so this is the most likely Burgers vector of the perfect dislocation that the partials are derived from. The next shortest Burgers vector with an [0 1 0] component, [1 1 0], is over four times larger. In addition to 1/2 [0 1 0], leading partial dislocations of the form 1/2 [1 1 0] and 1/2 [1 2 0] could locate the displaced molecules at the appropriate sites. However, these Burgers vectors have only small components along [0 1 0] (~ 20 and ~ 30%, respectively).

The partial dislocations most likely to be responsible for the observed microstructure would therefore, be of the form

$$1/2\,[0\,1\,0] + 1/2\,[0\,1\,0] = [0\,1\,0]. \quad (4)$$

These dislocations would glide in the (0 0 1) plane and be of pure edge character if the interfaces move in a normal direction. The stacking fault energy which separates the leading and trailing partial dislocations would then be given by an expression of the form

$$\gamma = \frac{\mu\,\mathbf{b}^2}{2\pi\,r\,(1-\nu)} \quad (5)$$

(e.g. [11]) where r is the separation distance between the two interfaces and $\mathbf{b}$ is the Burgers vector. Estimates from Fig. 2 suggests that a value of 2000 Å is appropriate for r and assuming a Poisson's ration (ν) of 0.3 and a shear modulus (μ) of $4 \times 10^5\,\mathrm{Ncm}^{-2}$, which are values for polyethylene perpendicular to the fibre axis, the stacking fault energy would be about $0.3 \times 10^{-7}\,\mathrm{Jcm}^{-2}$. This value is much smaller than the stacking fault energies of metals (Ag = $1.6 \times 10^{-6}\,\mathrm{Jcm}^{-2}$, Ni = $2.4 \times 10^{-5}\,\mathrm{Jcm}^{-2}$ [12, 13]) which would be expected when the open nature of these structures is considered. In terms of individual interactions, this corresponds to an energy of about $10^{-3}\,\mathrm{eV\,molecule}^{-1}$. This value is considerably smaller than the value of $10.3\,\mathrm{kJmol}^{-1}$ (0.11 eV molecule^{-1}) quoted as the energy difference between the β and α structures [14].

The distinctly different crystal structure induced by this stacking modification conflicts

with the studies of Mnyukh [15] and Kilaigordsky [16, 17] who observe that the orientation relationships between transformed and parent phases are not well defined in organic crystals. Thomas [9] conversely notes that in the monomeric 1,8-dichloro-10-methylanthracene [18] all the symptoms of stress induced martensitic transformations are displayed, with orientation relationships that are well defined between the daughter and parent phases. It is apparent that the transformation product observed here could well be formed by a somewhat analogous shear mechanism.

Acknowledgements

References

1. J. M. THOMAS and J. O. WILLIAMS, *Progr. Sol. Stat. Chem.* 6 (1971) 121.
2. *Idem, Surface and Defect Properties of Solids* 1 (1972) 130.
3. *Idem, Chem. Comm.* 432 (1967).
4. *Idem, Molec Cryst. Liquid Cryst.* 9 (1969) 59.
5. J. R. FRYER and D. R. TEDSTONE, Proceedings of the Crystallography Conference, (Australian Academy of Science, Melbourne, 1974) p. 237.
6. D. G. HOWITT and G. THOMAS, *Rad. Effects* 34 (1977) 209.
7. M. T. ROBINSON and G. E. KLEIN, *J. Amer. Chem. Soc.* 74 (1952) 6294.
8. M. ASHIDA, N. UYEDA and E. SUITA, *Bull. Chem. Soc. Jap.* 39 (1966) 12, 2616.
9. J. M. THOMAS, *Phil. Trans. Roy. Soc. A.,* 277 (1974) 251.
10. J. P. HIRTH and J. LORTHE, "Theory of Dislocations", (McGraw Hill, New York, 1968).
11. G. W. GROVES and A. KELLY, "Crystallography and Crystal Defects", (Longmans, Harlow, 1970).
12. D. J. H. COCKAYNE, M. L. JENKINS and I. L. F. RAY, *Phil Mag.* 24 (1971) 1383.
13. P. S. DOBSON, P. J. GOODHAW and R. E. SMALLMAN, *ibid.* 16 (1967) 9.
14. J. H. BEYNAN and A. R. HUMPHRIES, *Trans. Farad. Soc.* 51 (1955) 1065.
15. Y. U. MNYUKH, *J. Phys. Chem. Sol.* 24 (1963) 631.
16. A. I. KILAIGORODSKY, *Acta Cryst.* 18 (1965) 588.
17. *Idem,* "Molecular Crystals and Molecules" (Academic Press, New York and London, 1973).
18. J. O. WILLIAMS, *J. Mater Sci.* 8 (1973) 1361.