Observations on Dislocations in Tetraphenyltin and Its Isomorphs

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Examination of the characteristic pits produced by etching natural and mechanically damaged crystal surfaces shows that these are formed at the ends of dislocation arrays. Etch-pit shape, symmetry, and patterned arrays indicate that tetraphenyltin is a plastic, organometallic crystal with dislocation glide in {110} planes. The [001] direction is the most likely slip direction and the direction of the Burgers vector.

THE crystallography of plastically deformed molecular crystals was pioneered by Mügge and Johnsen.[1,2] Sherwood, Thomas, Williams, and others [3] have shown that organic solids contain many of the same structural imperfections found in metals and ionic crystals. Consequently, organic compounds are often used as 'metallic analogues.' They provide the opportunity to study the crystallography of slip, twinning, and cleavage in crystals of lower symmetry, which are uncommon in metals.[4] White tin, for example, is the only non-radioactive element possessing a body-centred tetragonal structure.[5] One possible metallic analogue for this element is the organometallic compound tetraphenyltin.

This communication reports on the favourable crystallographic planes and directions in which dislocations may move in this material and on the configurations of patterned dislocations that occur. These data permit comparisons to be made with the slip systems in white tin and conclusions to be drawn about the mechanical properties of other isomorphic compounds in this family.

Crystallographic Considerations.—Tetraphenyltin is isostructural with tetraphenyl-methane, -silicon, -germanium, and -lead.[6] It has unit-cell dimensions $a = 11{\cdot}85$ Å, $c = 6{\cdot}65$ Å, with space-group symmetry $P\bar{4}2_1c$.[7-10] Figure 1 shows the disposition of molecules in the unit cell. There are two molecules to the unit cell and each molecule has $\bar{4}$ symmetry. Compaction along the c-axis gives rise to a structure in which the four planar phenyl groups of each molecule fit closely

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Plate.1

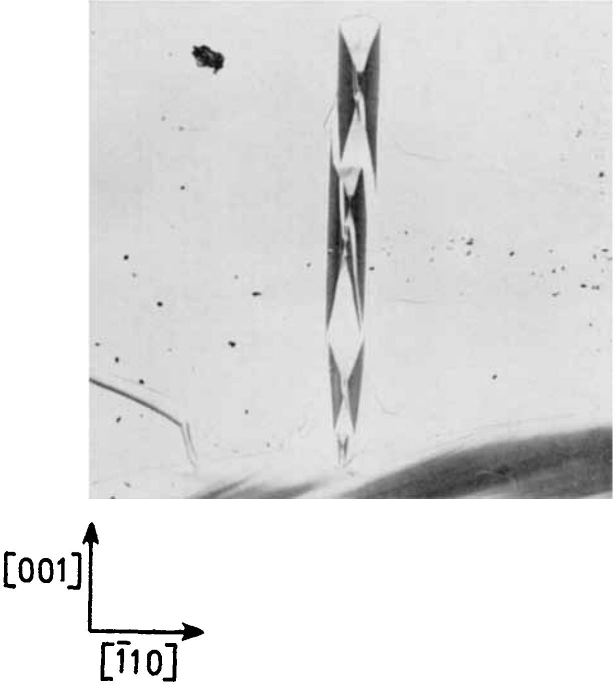

PLATE 1 Dislocation features on a natural (110) face. Dislocations occurring on these pits are introduced and aligned in the crystal during growth as a result of mechanical and thermal stresses: magnification ×100

PLate . 2

PLATE 2 Dislocation arrays on a (110) face developed by squeezing the crystal perpendicular to the [001] direction. Dislocation glide occurs on {110} planes in the [001] direction: magnification ×100

Plate . 3.

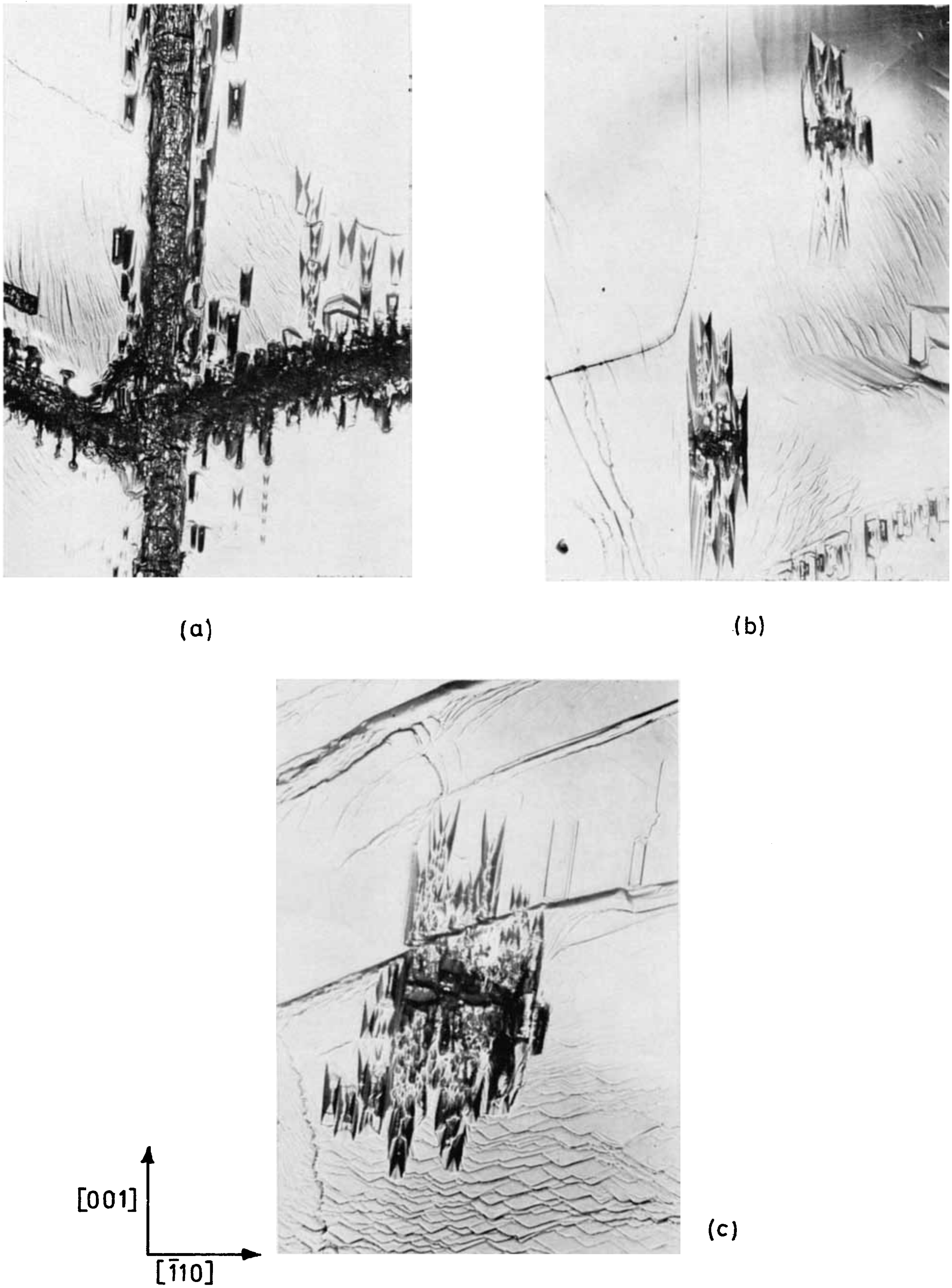

PLATE 3 Dislocation patterns produced on a (110) cleaved face by (a) mechanical scratching, (b) a hardness indenter, and (c) a 1 mm diameter steel ball. Compared with metallic or ionic crystalline materials, dislocations in tetraphenyltin are more easily introduced, moved, and multiplied; magnification × 100

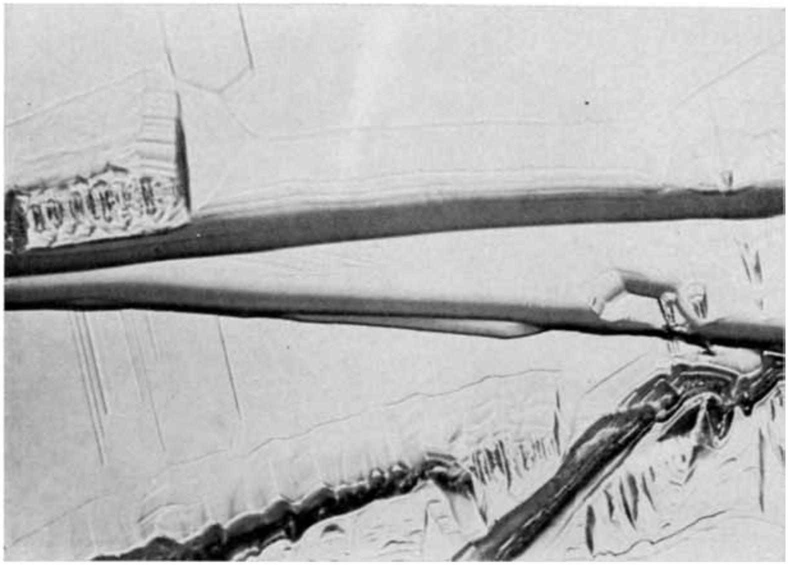

Plate.4.

Plate 4 Linear dislocation alignments arranged on a (110) cleavage face by small angle boundaries in a typical crystal; magnification × 200

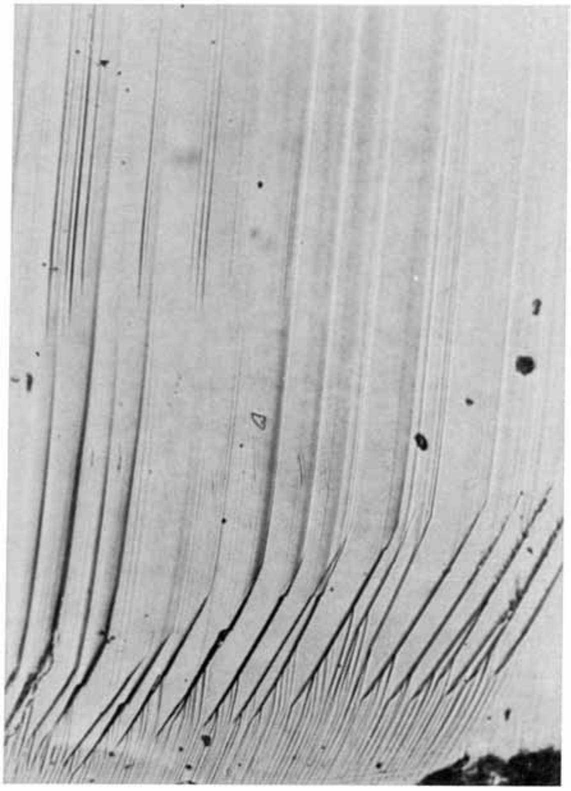

Plate 5

Plate 5 Increase in the cleavage step density on a (110) cleavage face for a crack crossing a boundary in a crystal of tetraphenyltin. The 'river line' pattern develops when the cleavage crack, instead of following a single crystal plane, is broken up by the structural defects at the boundary; magnification × 200 into the interstices between the phenyl groups of its neighbour. The intramolecular forces are strongly covalent, whereas the intermolecular binding is of the non-directed van der Waals type. It is therefore to be expected that molecules should easily slip past one another parallel to the *c*-axis and with more difficulty on planes inclined to this axis. Possible slip planes are of the *hk*0 type, probably {100}, which have a distance of 11·85 Å in the structure, and {110}, which is nearly close-packed and has $d = 8{\cdot}39$ Å. Structurally, crystals should cleave more easily parallel to the *c*-axis along {110} planes, rather than perpendicular to it, as has been found.

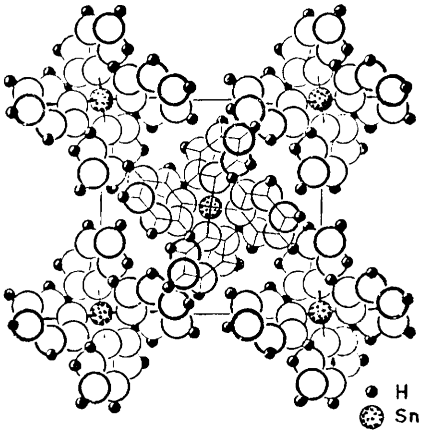

FIGURE 1 Disposition of tetraphenyltin molecules in the unit cell of the crystal structure. Projection of the structure is on *ab* with the atoms shown by spheres of arbitrary radius. Both cleavage and slip should be easiest parallel to the *c*-axis and more difficult on planes inclined to this axis (after Kitaigorodskii, ref. 6)

EXPERIMENTAL

Single crystals of tetraphenyltin were grown by slow cooling of saturated organic solutions as described elsewhere.[11] Figure 2 depicts an idealized crystal and shows the relationship between the external morphology and the orientation of the crystallographic axis. The tetragonal prismatic habit and optical axis are similar to KH_2PO_4 crystals, except that the prismatic faces are {110}. Many solvents and procedures were tried in an effort to develop the best method revealing the termini of dislocations at the faces. When care was taken to prevent the crystals from cracking, the most effective etchant was found to be chloroform. The procedure followed was to immerse the crystals in this etchant for 10 s and then quickly transfer the crystal into water at the same temperature. Vigorous agitation in the water-bath removed the etchant from the crystal surfaces. The surfaces were then dried with a soft tissue paper and photographed with conventional microscopy equipment. It was established, by the criteria usually employed in the etching technique, that the pyramidal dissolution pits produced by the immersion of the organometallic crystals in chloroform were nucleated at dislocation sites.[12-14] In as-grown crystals, the dislocation density varied from zero to 10^2 cm^{-2} depending on the conditions of growth.

Mechanical deformation was used to introduce glide dislocations into a crystal. This deformation was accomplished by several methods. A crystal was squeezed with a pair of tweezers, cleaved surfaces were scratched with a sharp needle, or indented by contact with a 1 mm diameter steel ball or a hardness tool.

The resulting dislocation etch pits were observed to form patterned arrays which may be tentatively assigned to three distinct categories: features formed during crystal growth, band of defects introduced by mechanical damage, and linear alignments arising from the existence of small-angle boundaries.

RESULTS AND DISCUSSION

Features formed during Crystal Growth.—Plate 1 shows some typical closely spaced pits aligned in the [001] direction that are occasionally developed on {110} faces of freshly grown crystals. It is believed that the dislocations occurring on these pits are introduced and aligned during growth either as a result of stresses from unequal heating of the crystal or from stresses caused by attachment of the crystal to the walls of the growth vessel. These pits appear to be bounded by faces oriented to within a few degrees of {111} and {101} surfaces.[15]

Defects introduced by Mechanical Damage.—Plate 2 shows that close to the edge of the squeezed crystal a row of shallow pits frequently arises running along the [001] direction and perpendicular to the direction of squeezing. Motion perpendicular to the glide plane indicates that the dislocations are changing glide planes with a resultant dispersion of the band. Matched rows of shallow pits are often visible on separated faces, suggesting that dislocation half-loops are introduced into the crystal during the

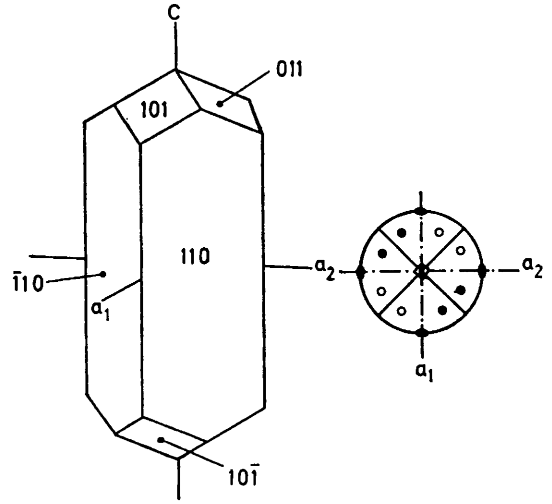

FIGURE 2 Schematic drawing of an idealized crystal of tetraphenyltin showing the relationship between the external morphology and the crystallographic and symmetry elements of the crystal class

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damage process. This observation is supported by the fact that continued etching also causes the centres of two adjacent pits to merge.

Plate 3(a—c) shows the dislocation patterns produced when cleaved (110) surfaces are mechanically damaged by (a) drawing a pointed needle across the surface, (b) by a hardness indenter, and (c) a 1 mm diameter steel ball dropped from a height of 3 cm. Again the etch pits align along the [001] direction and indicate the range of dislocation mobility in this material at room temperature. To assess the minimum stress required to produce dislocation multiplication at room temperature in this crystal system, a crystal was loaded with small weights and then re-etched. The load was progressively increased until multiplication of etch pits was obtained. The minimum stress required was found to be 500 g cm^{-2}.

Linear Alignment along Small Angle Boundaries.—Plate 4 shows a typical example of the linear array of dislocation etch pits delineating small angle boundaries in a typical crystal. The boundaries are curvilinear and probably consist of an interlacing of screw and edge dislocations.

Plate 5 shows a typical example of a ' river pattern ' on a (110) cleavage face. This line pattern, which contains a number of surface steps some as high as 1 μm, are produced whenever a crack proceeds across a small angle boundary consisting of screw dislocations not lying in the cleavage plane.

Conclusions.—These etch-pit shapes, symmetry, and patterned arrays permit us to conclude that tetraphenyltin is a plastic, organometallic solid with dislocation glide on {110} planes. The [001] direction is the most likely slip direction and the direction of the Burgers vector of the dislocations. This is also the experimentally observed slip system in white tin. Compared with metallic or ionic crystalline materials, dislocations in tetraphenyltin can be easily introduced, moved, and multiplied at room temperature by rather small stresses. This is understandable because of the lower shear modulus, lower thermal conductivity, higher diffusion, and higher thermal expansion coefficient associated with this class of compound. As the isostructural series progresses from tetraphenyl-lead to tetraphenylmethane, the crystal system becomes less anisotropic. It is expected therefore that along this series there will be a decreasing tendency for dislocation slip systems of the type normally encountered in crystals of body-centred cubic symmetry to occur in these tetragonal crystals.

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