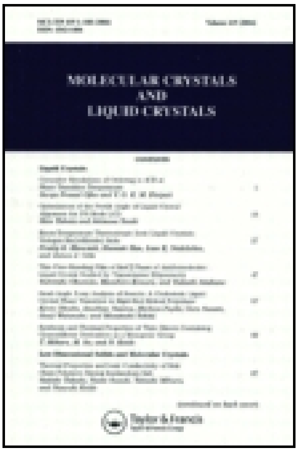

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Characterization of Defects in P-Terphenyl Single Crystals

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To cite this article: Michael Dudley , Rosemarie Disalvo , Shang-Yun Hou , Bruce M. Foxman & William Jones (1992): Characterization of Defects in P-Terphenyl Single Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 211:1, 35-42

To link to this article: http://dx.doi.org/10.1080/10587259208025802

Mol. Cryst. Liq. Cryst. 1992, Vol. 211, pp. 35–42
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Printed in the United States of America

CHARACTERIZATION OF DEFECTS IN *p*-TERPHENYL SINGLE CRYSTALS

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(*Received July 10, 1991*)

Abstract White Beam Synchrotron X-ray Topography has been used to characterize defects in solution-grown *p*-terphenyl single crystals. Defects observed include growth dislocations, mechanically introduced dislocations, macroscopic twins, twin lamellae, and dislocations emitted from twin boundaries. Line direction and Burgers Vector analysis of the growth and mechanically introduced dislocations, using projective geometry calculations and $\mathbf{g} \cdot \mathbf{b}$ analysis, respectively, are presented, along with complete analysis of the twin operation, obtained from a combination of analysis of optical micrographs and of orientation contrast on synchrotron topographs. The relationship between the Burgers vector of the dislocations generated at the twin boundary and the strain associated with the twins is discussed. Interesting interactions between mechanically introduced dislocations and twin boundaries are presented. Defect analyses are discussed in the context of results obtained previously using transmission electron microscopy.

Keywords: synchrotron topography, p-*terphenyl single crystals, dislocations, twinning, x-ray topography*

INTRODUCTION

It has been demonstrated by several groups that the technique of synchrotron white beam x-ray topography (SWBXRT) is particularly well suited for the study of defects in molecular single crystals.[1–3] The field of view in x-ray topography is orders of magnitude larger than that of its main competitor, transmission electron microscopy (TEM), and the interaction of x-rays with solids is much weaker than that of electrons so that large volume crystals can be studied (typically cm^2 in area and a fraction of a mm to 1-2 mm in thickness). This latter consideration enables defect structures in bulk single crystals to be readily determined.

Crystals of *p*-terphenyl, being relatively electron beam stable, were the subject of some of the pioneering work on the application of TEM to organic systems. The work of Jones[4] and Jones *et al* [5] on ≈300nm thick *p*-terphenyl crystals enabled the first direct study and detailed characterization of dislocations in organic solids. Operative slip systems were postulated to include: (001)[010], (001)[110], (001)[120] and, (100)[010]. Glide on (101) and (102) planes was also reported. Micro-twins, the twin plane of which was characterized to be (100), were also observed in this material. Previous studies on *p*-terphenyl by SWBXRT [6] revealed evidence for a high degree of distortion, with a mosaic spread of 7° being quoted. This seemed to indicate that this material is not amenable to this kind of study.

In this paper we report results of SWBXRT observations of defects in large *p*-terphenyl single crystals which contradict this latter indication. Comparison is drawn with the TEM results previously reported.[4,5]

EXPERIMENTAL

Crystals of *p*-terphenyl were grown at room temperature by self nucleation in slowly evaporating saturated toluene solutions. The crystals, which are monoclinic,[7] typically grew in the form of optically clear platelets with habit consisting of forms {001} (dominant) and {110}. Macroscopically twinned crystals were also grown, where the (001) crystal face is folded along [010] such that the (001) face normal for one half of the crystal is tilted by an angle of ≈37.5° with respect to that of the other half. This fact alone leads one to postulate a twin plane of (201). Examination of some crystals in the optical microscope revealed the presence of pairs of fine parallel lines, with trace running parallel to that of (201), i.e. along [010]. As will be shown later these correspond to pairs of twin lamellae which are of the same kind as the macroscopic twins.

SWBXRT was carried out on the White Beam Camera at the Stony Brook Synchrotron Topography Station on beamline X-19C at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The experiment consisted of placing the crystal at predetermined orientations in the path of the incident, area-filling white beam and collected the area-filling diffracted beams on the detector. The detector, which consisted of a cassette containing 8.5"×11" sheets of Kodak SR5 x-ray film, was typically placed normal to the incident beam direction at a distance of 10cm from the crystal. The longer wavelength components in the incident spectrum (λ >2.0Å), which do not contribute significantly to the diffraction patterns, were selectively filtered out using aluminum sheets. This prevented beam damage which became apparent after exposing to an unfiltered beam for periods in excess of ≈30mins (note a typical exposure with an unfiltered beam time is 5-10s).

Line direction analysis was carried out using a modified version of the projective properties algorithm of Miltat and Dudley.[8]

RESULTS AND DISCUSSION

Figure 1 shows a Laue pattern recorded from a macroscopically twinned crystal of *p*-terphenyl which was oriented such that one of two twin related regions had its large face perpendicular to the incident beam direction.

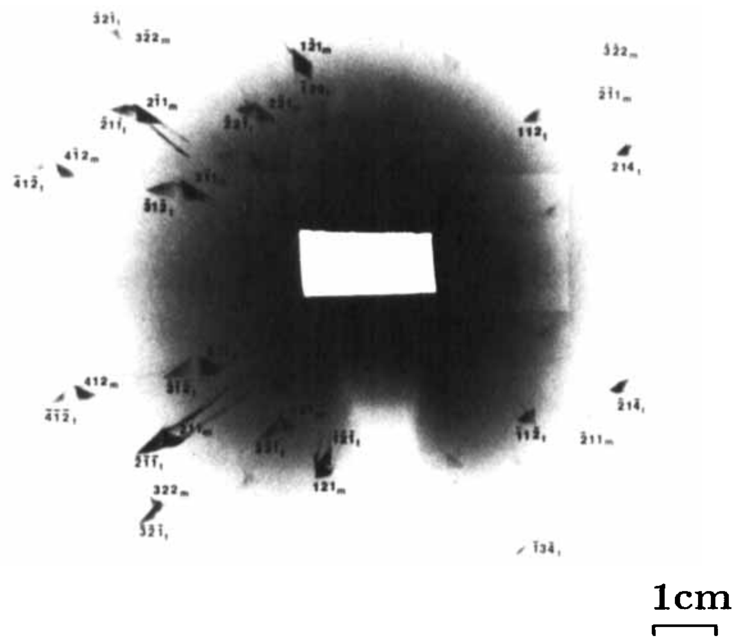

FIGURE 1. Indexed Laue pattern recorded from a macroscopically twinned crystal of *p*-terphenyl. Matrix reflection indices are indicated by subscript **m**, while twin reflections are indicated by subscript **t**. The incident x-ray beam is perpendicular to the (001) habit face of the matrix part of the crystal.

Note the presence of two independent Laue patterns. Detailed indexing of these individual patterns verifies the assignment of (201) as the twin plane. Further verification is obtained by the fact that the 201 reflection does not exhibit any orientation contrast (this reciprocal lattice vector coincides for matrix and twin). Note that observation of a (201) twin plane is in contradiction of previous reports by Jones,[4] who had suggested (100) as the twin plane. However, choice of (100) was made on the basis of the projected direction of twin images on TEM micrographs.

The projected direction of a (201) twin would in fact be the same, so that a (201) twin plane would have been equally plausible.

Figure 2(a) shows a 110 reflection recorded from a *p*-terphenyl single crystal containing straight growth dislocations, **G** and "wavy" mechanically induced dislocations, **M**.

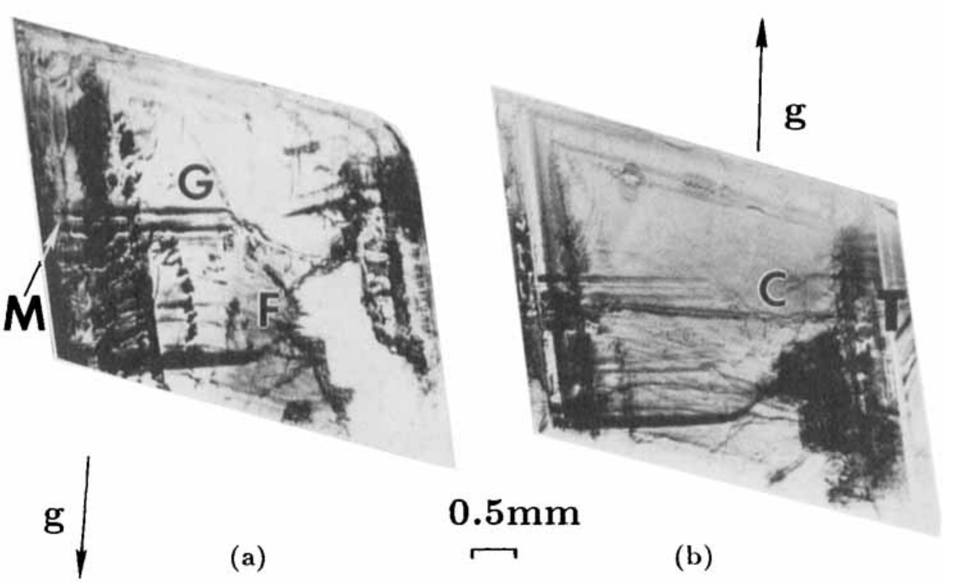

FIGURE 2. (a) 110 reflection recorded from a *p*-terphenyl single crystal, showing straight growth dislocations **G** and "wavy" mechanically induced dislocations **M**. Note also the misfit dislocations **F** associated with the included crystal which does not contribute to this image; (b) $2\bar{1}1$ reflection recorded from the same crystal. Note the presence of an image of the small included crystal, the absence of dislocations **M**, and the presence of small twin lamellae images **T**. **C** indicates a crack running across the crystal.

Dislocations **G** have line direction close to [120] and are of mixed character although no definite Burgers vector has yet been assigned (these dislocations are less frequently observed than the mechanically induced variety). The gap in the bottom right-hand corner of the figure is due to the presence of a second small crystal included in the parent crystal. No image from this small crystal appears with that of the parent crystal since the 110 reciprocal lattice vectors for the two crystals do not coincide. Note the misfit dislocations **F** which appear in the parent crystal to accommodate the misfit between the two crystals. Figure 2(b) shows a $\bar{2}11$ reflection recorded from the same crystal. First, note that an image is now evident from the small included crystal, since in this case the $\bar{2}11$ reciprocal lattice vectors for both crystals coincide. Second, note the absence of dislocations **M**. Small twins, **T**, with trace [010] also become evident on this image. The presence of dislocations **M** on figure 2(a) and their absence on figure 2(b) can be interpreted, using $\mathbf{g} \cdot \mathbf{b}$ analysis, to indicate that the operative Burgers vector is [120]. Line direction analysis, which can only be approximate since the dislocation segments are curved, and the long projected lengths of the dislocations indicate that the dislocations lie on (001). The slip system (001)[120] is in agreement with previous TEM studies.[5]

Figure 3 shows an enlargement of a detail from figure 2(a). Note the interaction between dislocations **M** and **G** causing a change in curvature of the former. This implies that dislocations **M** were introduced after dislocations **G**, probably as a result of handling (*p*-terphenyl crystals are extremely fragile).

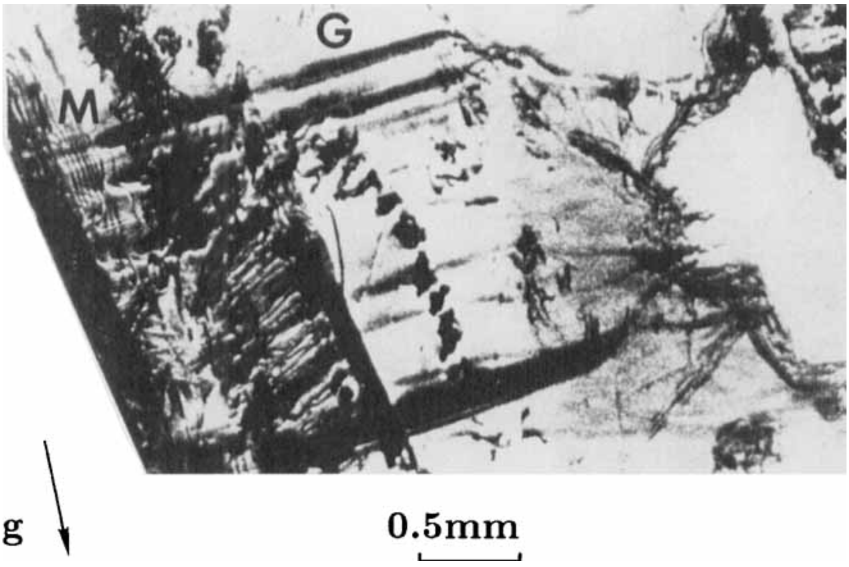

FIGURE 3. Enlarged detail from figure 2(a), showing interaction between mechanically induced dislocations **M** and growth dislocations **G**.

Figure 4(a) shows a $2\bar{1}1$ topograph recorded from a crystal containing twin lamellae, **T**, dislocations which have apparently been emitted by the twins, **E**, and mechanically induced dislocations, **M**, which appear to have originated at the mounting point located on the middle right of the image. The progress of dislocations **M** has been impeded by the twins **T**. As mentioned earlier, the twin lamellae **T** were each visible in the optical microscope as two fine, parallel lines running along [010] (i.e. the same trace as (201)), separated by a distance of ≈65μm. If this pair of lines corresponded to a single 65μm wide lamella, the lamella would be large enough to diffract independently, and the twin would be visible via orientation contrast. However, no such orientation contrast is visible on figure 4(a), with dark extinction contrast, originating from strain associated with the twins, being the only kind visible. It therefore appears that twin lamellae exist in *p*-terphenyl as closely spaced pairs. This presumably minimizes the energy associated with lattice distortion, although some finite distortion remains giving rise to the observed extinction contrast. Figure 4(b) shows an 201 image recorded from the same crystal.

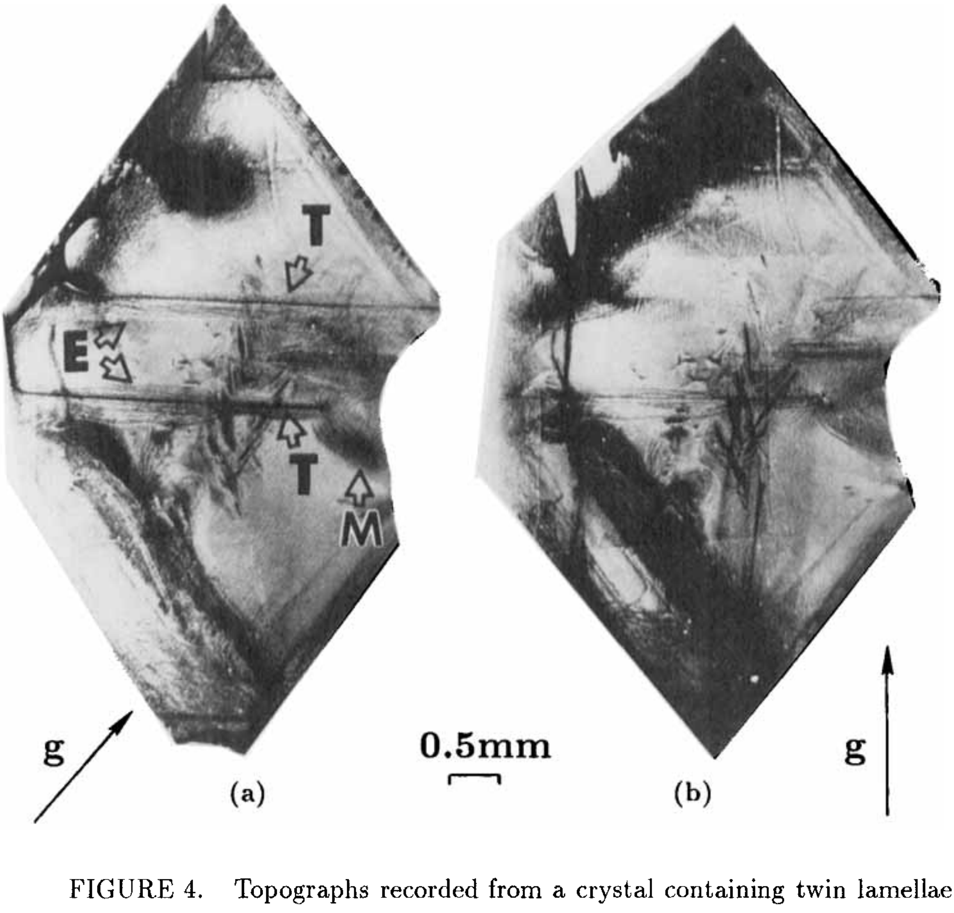

FIGURE 4. Topographs recorded from a crystal containing twin lamellae; (a) $2\bar{1}1$ reflection showing extinction contrast from twin lamellae, **T**, dislocations which have apparently been emitted by the twins, **E**, and mechanically induced dislocations **M**; (b) 201 reflection. Note the absence of the extinction contrast from the twins, as well as the absence of many of the dislocations **E**.

Note the absence of the contrast from the twins **T** on figure 4(b), confirming an assignment of (201) as the twin plane. Note that the majority of the dislocations emanating from the twin have also disappeared on this reflection but that a few remain. Those that disappear have a Burgers vector which lies in the twin plane. Likely possibilities are $[\bar{1}02]$ (which is the direction of shear which converts the matrix lattice to the twin lattice) and [010], but the former of these is eliminated by the visibility of the dislocations on the $2\bar{1}1$ reflection shown in figure 4(a). Line direction analysis on several of the curved sections of these latter dislocations indicates that they lie on (001), with average line direction [010], so that they are almost pure screw dislocations. This slip system, (001)[010], was also observed by Jones *et al.*[5] The segments of dislocation associated with the twin which do not disappear on the 201 reflection are also shown by line direction analysis to lie on (001). Possible Burgers vectors in the basal plane are: $[1\bar{1}0]$, [110], $[1\bar{2}0]$, [120] (all of which were observed by Jones *et al* [5]) and [100] (which was not observed by Jones *et al* [5]). The dislocations of interest are visible on 110, $\bar{1}10$, 211 and $2\bar{1}1$ reflections discounting $[1\bar{1}0]$, [110], $[1\bar{2}0]$ and [120], respectively, as possible Burgers vectors. To verify the remaining possibility, [100], it is necessary to record reflections from planes belonging to the [100] zone. This is made difficult in *p*-terphenyl by the absence of high structure factor reflections belonging to this zone which are accessible in transmission from a (001) surface orientation crystal. However, it was possible to record a (002) topograph in Bragg reflection geometry although image foreshortening made it difficult to extract absolutely conclusive information. Nevertheless close examination of this image appears to indicate that the dislocations of interest had, in fact, disappeared, as did all of the other dislocations, as would be expected for basal dislocations. This evidence leads one to conclude that a likely Burgers vector for the dislocations in question is [100], which when taken with their approximate line direction of [010], makes them almost pure edge dislocations. The screw and edge dislocations emitted from the twins will enable partial relaxation of the in-plane stresses associated with the twins in the perpendicular [010] and [100] directions, respectively. Preliminary investigation of the molecular configurations associated with a (201) twin indicate that the twin operation does not require any bending of the molecular axis (which lies parallel to the twin plane, approximately along $[\bar{1}02]$), but does require some anomalous rotations about the molecular axis. These latter rotations inevitably give rise to the lattice distortion visible via extinction contrast on figure 4(a). A more detailed analysis of the molecular configurations associated with a (201) twin is underway.

No evidence in this work was found for the non-basal dislocations observed by Jones *et al*,[5] although this is perhaps not surprising since these dislocations were observed to comprise low angle boundaries, which were totally absent in our crystals.

ACKNOWLEDGEMENTS

Research supported by the donors of the Petroleum Research Fund which is administered by the American Chemical Society (M.D. and R.D.). Topography carried out at the Stony Brook Synchrotron Topography Station, Beamline X-19C at the NSLS, which is supported by DOE under grant number DE-FG0284ER45098. B.M.F. acknowledges support from NSF under grant number DMR 8812427.

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