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SYNCHROTRON TOPOGRAPHY OBSERVATIONS OF A LOW TEMPERATURE PHASE TRANSITION IN AN ORGANIC CRYSTAL

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Abstract *In situ* observations have been made, using synchrotron white beam X-ray topography in conjunction with a specially designed liquid nitrogen cold-finger cryostat, of single crystals of *p*-terphenyl as they undergo a phase transition at ≈130K. The transformation involves a monoclinic to triclinic structural change. Direct observation was made of two kinds of domains in the low temperature phase. The original microstructure of the crystal appeared unperturbed despite the considerable strain which develops during the transition. Comparison is drawn between the X-ray results presented here and those obtained previously using transmission electron microscopy.

Keywords: synchrotron topography, low temperature phase transition, p-*terphenyl single crystals, laue pattern, cryostat*

INTRODUCTION

Monitoring the microstructure of single crystals while they undergo solid state phase transitions has been of interest to scientists in a variety of disciplines over a period of many years. Originally, many studies of this nature were carried out by metallurgists who considered the role of dislocations in solid state phase transitions in metals.[1–3] More recently, materials scientists and chemists have shown interest in examining microstructural, as well as structural detail in molecular single crystals undergoing solid state phase transitions, as well as those undergoing solid state reactions.[4–10] Microstructural details which have been of interest in these latter studies include observations of the formation of domain structures,[4,5] investigation of the role played by crystal defects during phase transitions and reactions,[9,10] and observations of defect generation accompanying transitions.[5]

Apart from a few brief electron microscopy studies[11,12] no systematic microstructural study of low temperature phase transitions in organic crystals has been

carried out. In this paper we present results of preliminary studies of the low temperature phase transition experienced by *p*-terphenyl single crystals. These studies were carried out *in situ* using synchrotron white beam x-ray topography (SWBXRT) which is particularly well suited to studies of single crystals undergoing phase transitions. The wavelength dispersion inherent to the Laue technique along with the high photon flux of an area-filling synchrotron beam mean that both detailed structural and microstructural studies can be conducted over a wide temperature range. The broad range of wavelengths available also provides a good degree of tolerance to lattice distortion which might be encountered on passing through a structural change.

The transition in *p*-terphenyl, which occurs on cooling at ≈130K, is characterized by a monoclinic to triclinic structural change, although it has been shown by Baudour *et al* [13] that it is more convenient to choose a pseudo-monoclinic unit cell for the low temperature phase. Despite this latter choice of unit cell, the decrease in symmetry which accompanies the transition is nevertheless characterized by a loss of the glide plane associated with the room temperature space group, $P2_1/a$. However, Baudour *et al* [13] found that in the low temperature phase, the intensities of hkl and $h\bar{k}l$ reflections were equal. It was argued that this requires the existence of two sorts of domains, related by a glide plane, which are equally probable, although no direct evidence was found for their existence. Jones *et al* [11] interpreted a variation of intensity as a function of position on a bend contour recorded by TEM at ≈100K as being indicative of the presence of at least two domains. The difference in structure factor for the operative reflection in the two domains was postulated to account for the intensity variation. White beam topography, with its ability to yield both structural and microstructural information, should be well suited to investigate the existence of these low temperature domains.

EXPERIMENTAL

Single crystals of *p*-terphenyl were grown at room temperature by self nucleation in saturated toluene solutions. Crystals grew in the form of plates, typically a few mm across and 200-300μm thick. Occasionally, macroscopically twinned crystals were produced.[14]

Topography was carried out using the area-filling synchrotron white beam available on the Stony Brook Topography Station on beamline X-19C at the National Synchrotron Light Source, at Brookhaven National Laboratory. Aluminum filters were used to prevent beam damage.[14] The crystals were mounted using mylar bags

inside a specially designed copper cold-finger cryostat system. The body of the cryostat consisted of a double-walled evacuated glass vessel, the outside of which was further insulated with styrofoam. Sheets of mylar were used as windows to allow the x-rays to enter and leave the system. The use of multiple layers minimized problems with freezing of condensed water vapor. Temperature in the vicinity of the crystal was measured with a thermocouple and controlled digitally to an accuracy of $\pm 0.5°$. The transmission Laue geometry was adopted, with the detector (a cassette containing 8.5"×11" sheets of Kodak SR5 x-ray film) perpendicular to the incident beam direction, typically at a distance of 10cm from the crystal. Laue patterns were indexed using specially designed computer software.

RESULTS AND DISCUSSION

Figure 1 shows a white beam Laue pattern recorded at room temperature from a *p*-terphenyl single crystal mounted inside the cryostat. Indexing was carried out using published lattice parameters.[15] Figure 2 shows a Laue pattern recorded at a temperature of 120K. Note the appearance of "double images". Analysis of the "average" positions of these pairs of reflections enables indexing using the pseudo-monoclinic cell parameters. However, the presence of the double images can be explained by the existence of the two types of domain postulated by Baudour *et al.*[13] For example, for a Laue pattern indexed using the pseudo-monoclinic unit cell, hkl and $h\bar{k}l$ are equivalent reflections which are related on a transmission Laue pattern, recorded with the beam normal to (001), by mirror symmetry (in actual fact the symmetry element is an a-axis glide plane, but this is indistinguishable from a mirror plane on a Laue pattern). In the actual low temperature structure, which is triclinic, this mirror symmetry is lost. However, the intensities of hkl and $h\bar{k}l$ reflections were still found by Baudour *et al* [13] to be equal. This was explained by the prediction of the existence of two domains in the low temperature structure related by an a-axis glide plane. Adding the intensities of the "double" reflections observed on figure 2 would give the impression that hkl and $h\bar{k}l$ intensities were equal. In actual fact each "double" reflection is made up of a non-equivalent pair of reflections, one from α phase and the other from β phase, as can be seen from the indexing on figure 2, which is carried out assuming that the actual triclinic unit cell deviates only slightly from the pseudo-monoclinic cell. Analysis of the indexed pattern verifies that the mirror plane relating the two domains, which is observed from the symmetry of the Laue pattern, is in fact (010), in agreement with the a-axis glide plane predicted by Baudour *et al.*[13] As expected, reflections

belonging to the [010] zone, which would be exactly perpendicular to (010) in a true monoclinic structure, but slightly tilted away from perpendicularity in the related triclinic structure, show minimum (in fact unresolvable) spatial separation between the pairs of reflections.

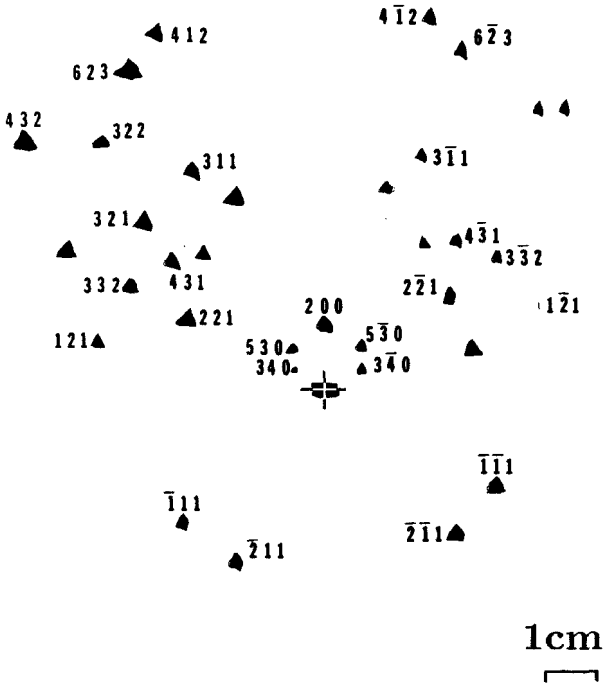

FIGURE 1 Indexed transmission Laue pattern recorded at room temperature from a *p*-terphenyl single crystal mounted inside the cryostat. The cross indicates where the direct beam hit the beam stop on the film.

No lateral resolution of individual domains is observed, probably due to the fact that they are below the resolution limit of the technique which is around 1-2μm. The crystal does however appear to be strained in its low temperature form, as indicated by the asterism in the Laue pattern. This may be due to the local mismatch which exists between adjacent domains, which appear to form a finely dispersed solid solution. The asterism, or change in size and shape of the individual diffraction spots, appears to be anisotropic on the pattern. The nature of this anisotropy indicates that in fact the crystal is bending, so that reflections with reciprocal lattice vectors close to the bending axis are relatively undistorted, while those with vectors close to being perpendicular to the axis appear highly distorted.

It is probable that this high degree of strain would lead to line broadening which would make it difficult to resolve closely spaced diffraction peaks from the α and β structures on a single crystal diffractometer. Laue diffraction with its wavelength dispersion is able to tolerate this lattice distortion, while maintaining sufficient angular resolution to distinguish between the two phases.

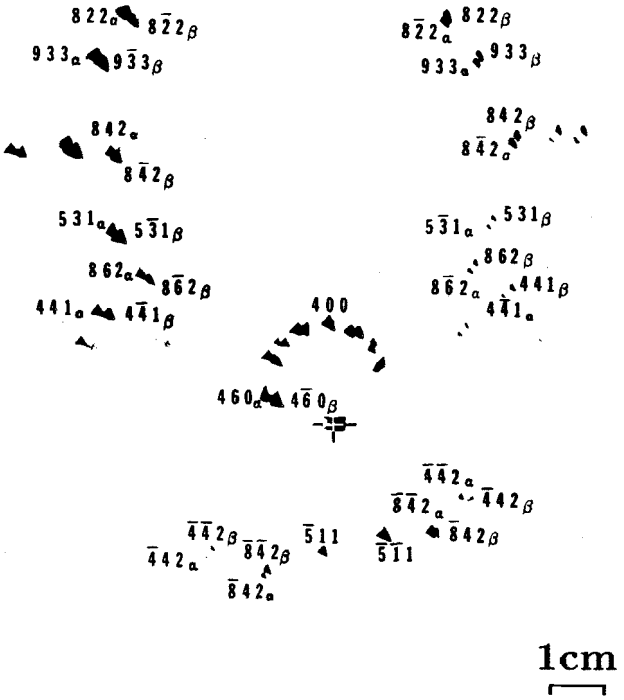

FIGURE 2 Indexed Laue pattern recorded at 120K from the same *p*-terphenyl single crystal. Again the cross indicates the direct beam position. This pattern consists of a superposition of patterns from the α and β low temperature phases.

As the crystal is warmed to room temperature, the original Laue pattern is recovered some 50-60K above the original transition point, indicating some difficulty in nucleating the room temperature phase in the low temperature one. Examination of individual images reveals that there appears to have been no significant change in microstructure. This indicates that the strain which becomes evident in the low temperature phase is relaxed when the crystal is taken back to room temperature. The fact that no defects were generated by the strain means that it was entirely elastic. Strain in the low temperature phase was also observed by

Jones *et al*,[11] who attributed it to the coexistence of the two kinds of domains. The lack of significant microstructural change is demonstrated by examination of figure 3 which shows the 200 reflection from the room temperature phase before and after cycling several times through the transition. The microstructural detail which was present before the transition consisted of dark lines parallel to one edge of the crystal which are associated with surface steps on the crystal which are visible in the optical microscope. Apart from these features the crystal was essentially defect free prior to the transition. The contrast from the surface features appears identical following the transition. However, one new feature does appear after the transition, i.e. the curved feature at the bottom of figure 3(b). This feature only appears on the one reflection on both this Laue pattern, and all subsequent Laue patterns, and as such is not readily identifiable. The origin of this contrast feature is still under investigation. Further parallel studies are currently being carried out on crystals containing higher dislocation densities and crystals containing twins.

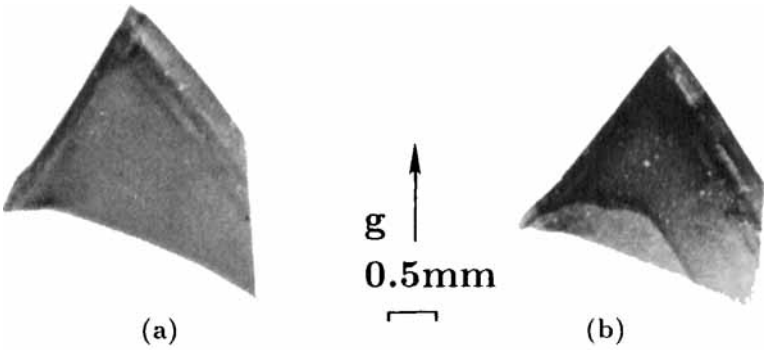

FIGURE 3 Enlargement of the 200 reflection (a) from figure 1, and (b) from a similar Laue pattern recorded at room temperature after cycling through the transition.

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