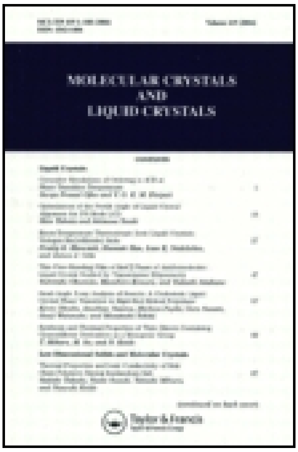

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SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY CHARACTERIZATION OF DEFECT STRUCTURES IN 2,10-UNDECANEDIONE/UREA INCLUSION COMPOUNDS

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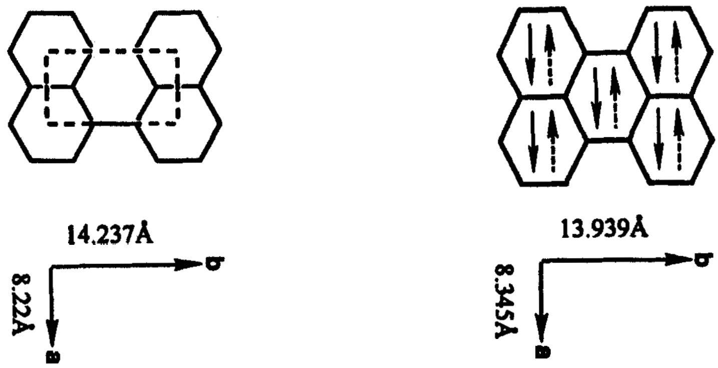
Abstract The defect structure of a crystal of the urea inclusion compound (UIC) of 2,10-undecanedione was investigated using Synchrotron White Beam X-ray Topography. X-ray transmission topographs recorded from different regions show that the crystal is divided into several twin domains. Each region in the crystal is revealed on the topographs by orientation contrast arising from the mutual misorientation of adjacent regions. Using a combination of pinhole Laue pattern analysis and topographic orientation contrast analysis, the twin operation was determined to be consistent with an approximately 60° rotation about the orthorhombic *c*-axis. Possible twin boundary structures are also presented. Other defects such as dislocations and inclusions are also characterized.

INTRODUCTION

Channel inclusion compounds of urea continue to present significant challenges to solid state chemists and crystallographers. For the majority of UICs, the urea host molecules pack in a hexagonal host structure (space group $P6_122$) that forms linear, non-intersecting channels parallel to the crystallographic *c*-axis. Within these channels, long chain molecules such as linear hydrocarbons are arranged in their zig-zag conformations.[1] The structural periodicities of the host and guest molecules are generally incommensurate along the channel axis. That is, there are no integers m and n that satisfy the relationship $mc_g = nc_h$, where c_g is the repeat length of the guest molecule and c_h is the repeat length of the host. Crystals of 2,10-undecanedione/urea exhibit a different structure from most urea inclusion compounds.[2] In the first place, the host and guest molecules conform to the commensurate relationship $2c_g = 3c_h = 33.0$Å. Secondly, the host structure is distorted from the normal hexagonal UIC structure to an orthorhombic structure (space group C222$_1$). The unit cell is elongated by 0.12Å (from 8.22Å to 8.34Å) along the *a*-axis and compressed along the *b*-axis by 0.3Å (from 14.24Å to 13.94Å). Figures 1(a) and (b) are schematic diagrams showing the normal hexagonal and distorted orthorhombic host structures.



(a) (b)

FIGURE 1. Schematic diagrams showing the (a) normal hexagonal and (b) distorted orthorhombic host structures, where the solid arrow represents the direction of lattice distortion along the *a*-axis.

Extensive twinning in 2,10-undecanedione/urea inclusion compounds has been observed.[2] A comprehensive investigation of this phenomenon is important in developing a better understanding of structural requirements for the occurrence of twinning in crystals. In this paper, we present the nondestructive investigation of twin boundaries in 2,10-undecanedione/urea using Synchrotron White Beam X-ray Topography (SWBXT).[3,4] The broad wavelength range of the radiation utilized enables SWBXT to reveal the orientational relationships between twin related regions in crystals. Each twinned region is able to select different diffraction wavelengths, giving rise to topographic images that are split at twin boundaries. The natural collimation and large area of the synchrotron beam enable SWBXT to yield both microstructural (locations and shapes of twin domains) and structural (orientation relationship) information about large twinned crystals. SWBXT is therefore uniquely suited to the study of twinned crystals.

EXPERIMENTAL

Materials

An 8×8×0.2 mm^3 hexagonal plate (001) of 2,10-undecanedione/urea suitable for topographic analysis was obtained through evaporation of a methanolic solution of

2,10-undecanedione and urea over the course of several days. Although originally in the form of a hexagon, it was damaged during handling, resulting in a specimen of rather irregular shape.

SWBXT

SWBXT experiments were carried out at the Stony Brook Synchrotron Topography Facility, beamline X-19C, at the National Synchrotron Light Source, Brookhaven National Laboratory. All diffraction images were recorded on Kodak SR-1 high resolution X-ray film. The detector consisted of a film cassette placed perpendicular to the incident X-ray beam.

Pinhole Laue diffraction patterns in transmission were recorded from each twin-related region individually using an incident beam reduced in size to about $0.7\times 0.7\ mm^2$. In combination with topographic orientation contrast analyses carried out on images recorded with an area-filling $8\times5\ mm^2$ incident beam, these results reveal the relative orientation of adjacent twin domains. From these results the structures of the twin boundaries were readily determined.

RESULTS AND DISCUSSION

Figure 2 shows a transmission optical micrograph of a macroscopically twinned 2,10-undecanedione/urea crystal.

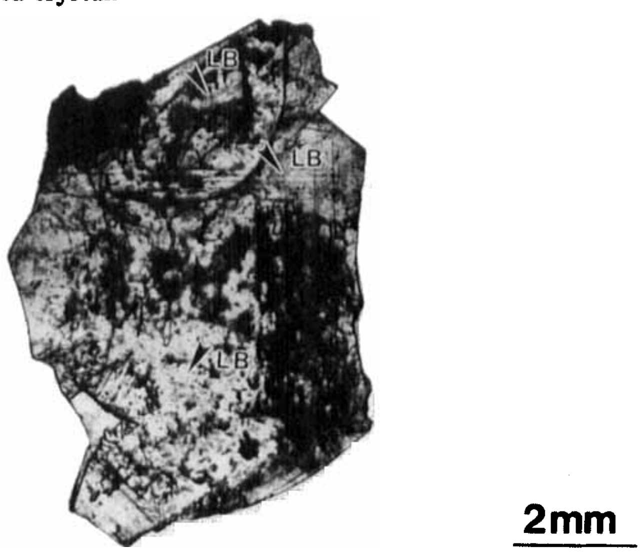


FIGURE 2. Transmission optical micrograph of the twinned 2,10-undecanedione UIC crystal showing lateral twin boundary (**LB**) configurations.

In this transparent sample both top and bottom surfaces can be imaged simultaneously, enabling the orientations of lateral twin boundaries to be determined from the relative positions of their intersections with top and bottom surfaces.[5] For the sample investigated here, the boundaries were found to lie perpendicular to the specimen surface.

Synchrotron White Beam X-ray Topography

Figure 3 (a) and (b) show topographic Laue patterns recorded from different regions of the crystal with the incident beam perpendicular to the sample surface. Twin configurations, directly observed via orientation contrast, were found to comprise both large-volume, macroscopic twins and thick twin lamellae. Upon detailed analysis, Figure 3 revealed that there were five superimposed diffraction patterns in the crystal studied. This indicated that the crystal was divided into five twin-related regions (indicated by $\mathbf{T}_1$ to $\mathbf{T}_5$) with different relative orientations.

To accurately determine the orientations of these twin related regions, pinhole Laue diffraction patterns in transmission were recorded as shown in Figure 4.

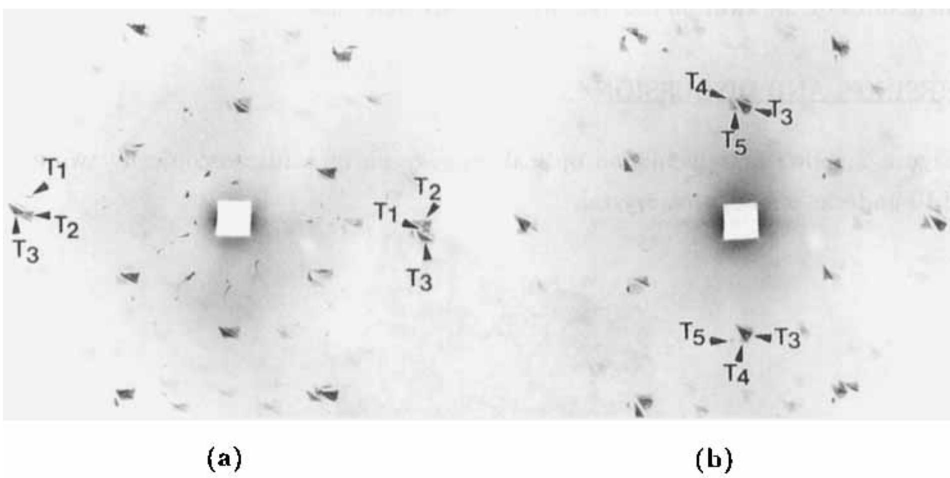


FIGURE 3. Transmission Laue diffraction patterns recorded from the 2,10-undecanedione UIC crystal. Five superimposed diffraction patterns indicated by $\mathbf{T}_1$ to $\mathbf{T}_5$ were observed.

As revealed by these patterns, adjacent regions are related to each other by an approximately 60° rotation (note that this angle would be exactly 60° if the system were hexagonal). This indicates that the twinning operation is consistent with an approximately 60° rotation about the crystallographic c-axis. These results are also consistent with optical studies of the birefringence of these crystals.[2]

Figure 5 shows transmission topographs recorded from different twin related regions using the composition planes separating the regions as the reflecting planes. It is worth noting that these topographs show the absence of orientation contrast. This indicates that the composition planes of adjacent twin related regions are coincident, although strain contrast associated with twin boundaries due to structural distortions is discernible.

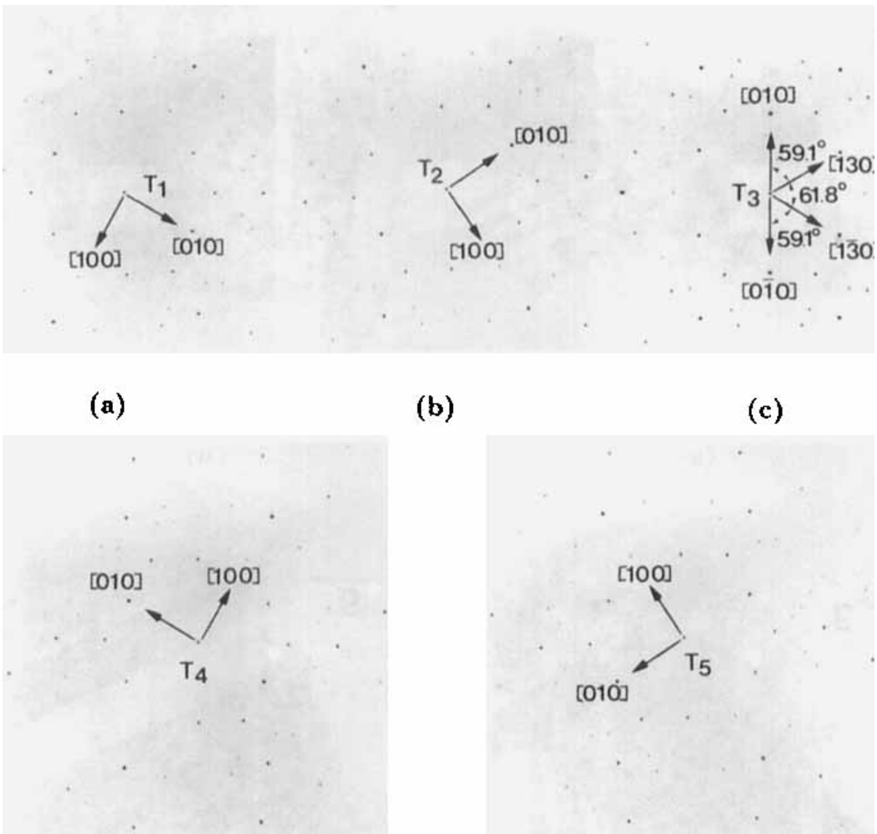


FIGURE 4. Pinhole Laue diffraction patterns recorded in transmission geometry from twin-related regions T_1 to T_5 respectively, showing orientation relationships between these regions.

The twin structure in this specimen can be represented using stereographic projections as shown in Figure 6. In this figure, the orientation relationships of these twin related regions are revealed; the contact points of these projections label the poles of the composition planes. The rotation angle, which would be exactly

60° if it were hexagonal, ranges from 59.1° to 61.8°, as determined by measuring the angles between the [010]-[130], [130]-[1$\bar{3}$0] and [1$\bar{3}$0]-[0$\bar{1}$0] directions from pinhole Laue diffraction patterns.

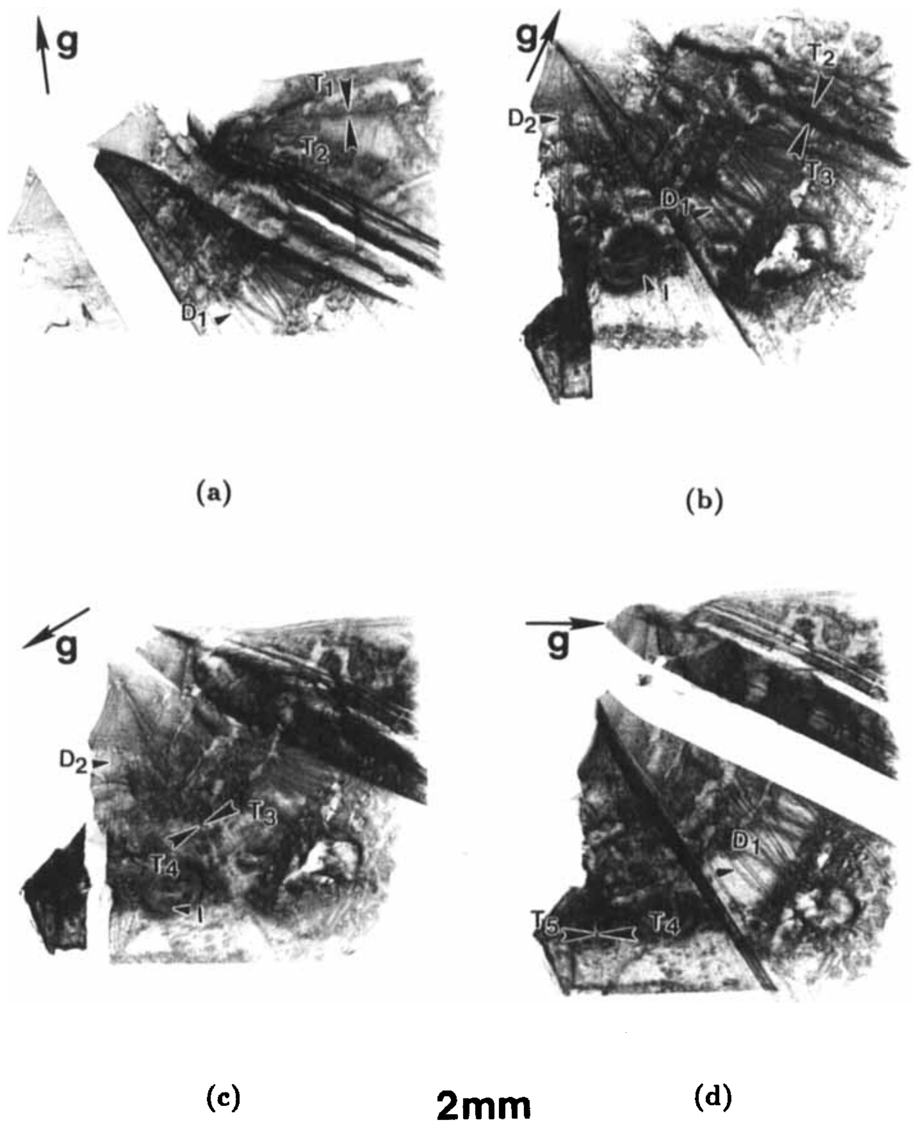


FIGURE 5. Transmission X-ray topographs recorded from (a) $\mathbf{T_1}$ and $\mathbf{T_2}$; (b) $\mathbf{T_2}$ and $\mathbf{T_3}$; (c) $\mathbf{T_3}$ and $\mathbf{T_4}$; and (d) $\mathbf{T_4}$ and $\mathbf{T_5}$ regions by using composition planes as the reflecting planes. Note the extinction of dislocations $\mathbf{D_1}$ and $\mathbf{D_2}$ shown in (c) and (d) respectively.

Other defects such as inclusions and dislocations (indicated as **I** and **D**, respectively) were also observed.

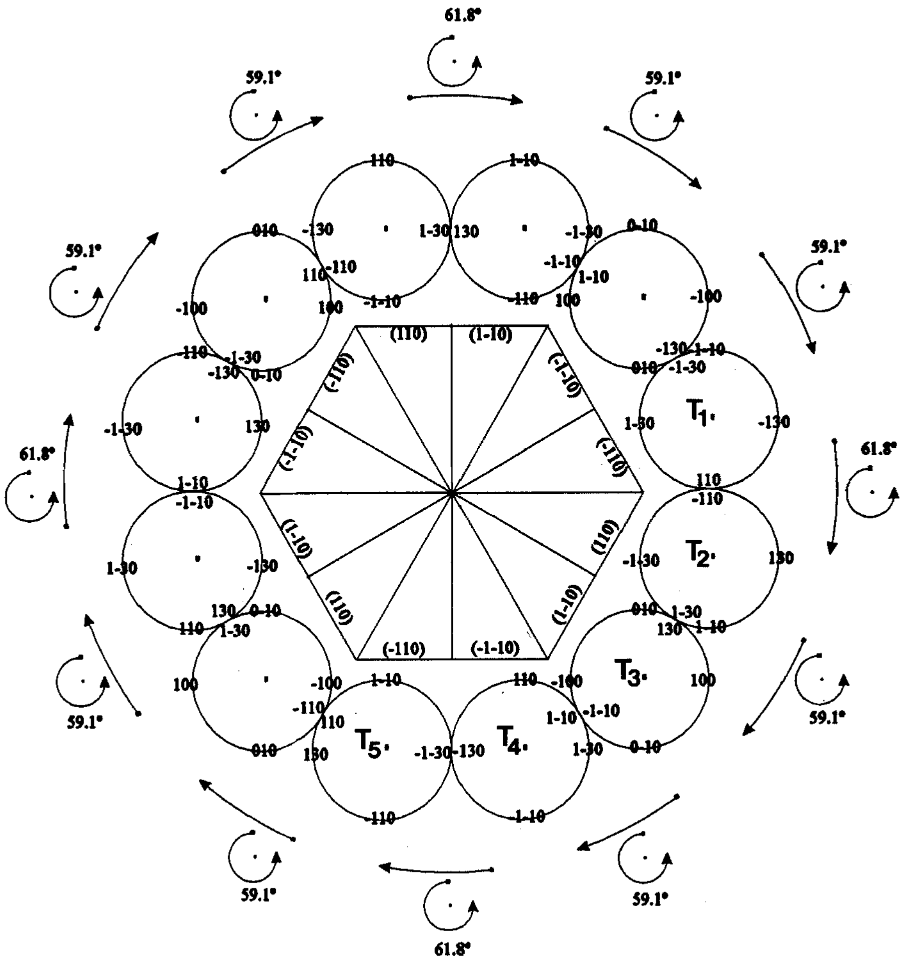


FIGURE 6. Stereographic projections showing twin structures in the 2,10-undecanedione UIC crystal. The contact points of these projections label the poles of the composition planes.

Detailed analysis of contrast variations of dislocations in different reflections shows that the dislocations are out of contrast when reflections with **g** vectors perpendicular to their line directions are used. By using the **g** · **b**=0 criterion,[4] one can determine that these dislocations are of screw character with Burgers vector parallel to the [130] direction.

Twin boundary structures

By analyzing twin boundary structures, one can gain an understanding of the structural requirement for the occurrence of twinning. Twinning appears in crystals where twin boundaries of good structural fit (i.e., low energy configuration) can be formed.[6]

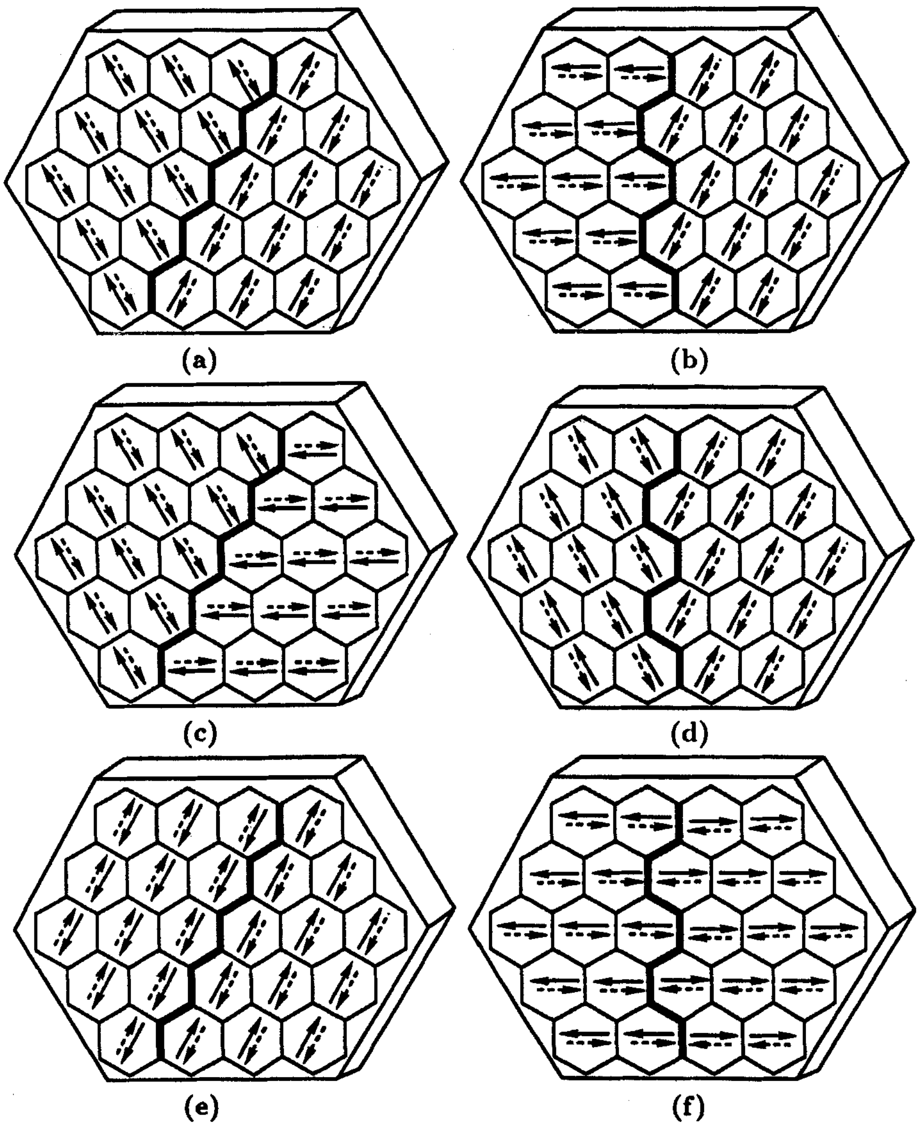


FIGURE 7. Schematic diagrams showing the structures of (a) (010)-(110); (b) (100)-(130); (c) (110)-($\bar{1}$10); (d) (130)-($\bar{1}$30); (e) (010)-(010); and (f) (100)-(100) twin boundaries.

In crystals with hexagonal or nearly hexagonal structures (such as 2,10-undecanedione UIC crystals), twin boundaries of good structural fit can exist in either of the two possible structural models (defined as **A** and **B** types). If one uses the orthorhombic description for a perfectly hexagonal system, there would be three equivalent **A** type boundaries lying along different (010)-(110), (110)-(110) and (010)-(010) lattice planes and three equivalent **B** type boundaries lying along different (130)-(130), (130)-(100) and (100)-(100) lattice planes. In the distorted 2,10-undecanedione/urea system, boundaries of lattice match can only occur along the (110)-($\bar{1}$10), (130)-($\bar{1}$30), (010)-(010) and (100)-(100) planes. The structurally mismatched (010)-(110) and (100)-(130) boundaries are disallowed. The six types of twin boundaries are schematically shown in Figures 7, where the solid arrow represents the direction of lattice distortion along the *a*-axis.

The twin boundaries associated with these different operations can be observed by X-ray topography via different contrast mechanisms. In (110)-($\bar{1}$10) and (130)-($\bar{1}$30) cases, twin boundaries arising from the mechanism described in Figure 6 were characterized via orientation contrast (lattices of twin related regions are in general not coincident). In the (010)-(010) and (100)-(100) cases, twinning can be introduced either by slipping one half a unit cell along the *c*-axis or by a 180° rotation along one of the two twofold axes. In this latter case, the lattices of twin related regions are exactly coincident, and so no orientation contrast would be expected, although this type of twinning could conceivably be revealed on X-ray topographs by strain contrast or by dynamical fringe contrast from the boundary itself. This type of twinning, however, was not observed.

Twinning and crystal growth behavior

2,10-undecanedione/urea crystals consist of twelve sectors related by sucessive rotations of approximately 60° about the orthorhombic *c*-axis. These sectors intersect at a point close to the center of the crystal, which corresponds to the location of the growth nucleus. The arrangement of these twins strongly suggests that twinning may occur in the very first stage of growth.

CONCLUSIONS

SWBXT is a powerful technique for the investigation of twinned crystals. Twin-related regions with mutual tilts of the lattice planes were imaged simultaneously in one exposure. Transmission Laue diffraction patterns provided a direct measure of the symmetry relationships between twin related regions. Information such as twin distributions, twin boundary configurations and twin operations can be obtained. This is important if one is to develop a better understanding of structural properties and kinetic processes associated with growth of twinned crystals. The twinning in 2,10-undecanedione/urea is consistent with successive rotations of approximately 60° about the orthorhombic *c*-axis. Because two different families of twin boundaries ({110}-{110} and {130}-{130}) are allowed, a total of twelve sectors are observed. Although the twin boundaries show good structural fit, strain contrast associated with twin boundaries is still discernible indicating that structural distortions exist in the neighborhood of twin boundaries.

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