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Observation of fine one-dimensionally disordered layers in silicon carbide

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Abstract

The improved resolution of synchrotron edge-topography is enabling thinner, (<100μm), silicon carbide crystals to be studied, and is providing a more detailed and wider database on polytype depth profiles. Fine long-period and one-dimensionally-disordered layers, 5-25μm thick, can now be confidently resolved and are found to be very common features, often in association with high-defect density bands. These features are illustrated in this paper using three examples. A new long period polytype LPP (152H/456R) has been discovered and reported here for the first time.

Silicon carbide has proved to be an interesting material, not just for its commercial value as a mechanical grinding medium or its potential in ceramic and high-temperature electronic applications, but also in that its prolific polytypism has attracted theorists and experimenters to study its remarkable behaviour. Polytypism (Baumhauer 1912) is the ability of a material to exist in different crystallographic forms which differ in one crystallographic direction: this can be achieved by variations in atomic layer stacking sequence so that unit cells, for different polytypes, become related by simple integral factors corresponding to the number of stacked layers between each repeat. Silicon carbide is notorious for its ability to form polytypes: several hundred are known, with c-repeats varying from 2 layers to many hundreds of layers. In the limit of no finite repeat, i.e. $c \rightarrow \infty$, the polytype assumes the extreme case of one-dimensional disorder.

The authors have previously emphasized (Fisher and Barnes 1984, 1990) the need to include an assessment of the spatial extent of polytypism and one-dimensional disorder in any complete description of the phenomena. X-ray diffraction topography is a technique that provides an opportunity to relate polytype content to features such as dislocations, defect configurations and crystal morphology. A crucial development in this quest has been the emergency of edge-topography, an otherwise little-used technique in which diffraction contrast is obtained in *reflection* from the *edge*, rather than the more substantial faces, of a crystal platelet. Fisher (1986) showed that synchrotron edge-topography could be effectively exploited to depth-profile the content of a multi-polytypic SiC crystal. The technique was, however, then limited to the study of well-defined crystals, usually of thickness greater than 300μm. In fact a study on over 200 crystals (Fisher and Barnes 1990) succeed in producing only 32 suitable edge-topographs, of which only 9 showed interesting features.

Following the high-brightness-lattice (HBL) upgrade of the Daresbury Synchrotron in 1986, many workers have confirmed the general improvements in topographic resolution. In addition to resolution there are other factors which determine the choice of geometry for edge-topography of a given material: these include recognition of polytype, overlap of reflections, ability to satisfactorily aperture a given edge and so on. The geometry of Mardix, Lang, Kowalski and Makepeace (1987) works well for single-polytype ZnS crystals. However, for complex multi-polytypic crystals of SiC, the geometry of Fisher and Barnes (1984) is more suited to depth-profiling from the edge topographs. Together with the general improvements offered by the HBL-synchrotron, this geometry is now enabling thinner crystals to be examined and resolving new features that have a significant bearing on the polytype history of the crystals. These findings are reported here for the first time.

Multi-polytypic silicon carbide crystals display syntactic coalescence: that is the growth of one polytype layer on top of another with exact atomic register across the common boundary (0001-plane). Consequently edge-topographs display a complex superposition of Laue-type diffraction patterns but with one simplifying feature: that each polytype sub-pattern is identically oriented.

Figures 1-3 illustrate three examples of what can be accommodated by current synchrotron edge topography. Figure 1(b) shows just part of the 314l - diffraction row from a complex multi-polytypic crystal which displays at least seven separate polytype layers, and has been assigned the combination 6H + 15R + 6H + 15R +15R +1DD + 6H as depicted in the model (fig 1(c)) and termed a '1DD-sandwich'. The nomenclature (Ramsdell 1947) refers to the number (here, 6 and 15) of basic h.c.p. layers in the unit cell, and cell type (H = hexagonal; R = rhombohedral); the designation 1DD by the authors denotes a one-dimensionally disordered layer, or at least a polytype with a period so long that it cannot be accurately measured or distinguished from complete one-dimensional disorder (e.g. > 3000 layers). The main features from fig. 1 could have been deduced from pre-HBL synchrotron topographs. Indeed two results, comparable to the sandwich in fig. 1 (c), were previously found and published (Fisher and Barnes 1990) from data obtained using the pre-HBL synchrotron. In those days the assignment of a 1DD-layer would have been made primarily on the basis that the *sum* of all the polytype layer thicknesses, as measured from the edge-topograph reflections do *not* equal the full crystal thickness: the remainder would have been accounted for by invoking the presence of a 1DD-layer, and the absence of a corresponding discrete reflection would have been accounted for by the streaking along diffraction rows. This is still the main basis for assignment. In this example, the six regular polytypes (6H, 15R, 6H, 15R, 15R, 6H) total 1100 μm, whereas the total crystal thickness is 1350μm, leaving a remainder of 250μm for the 1D-disordered layer.

Clearly this method assignment 'by absence' becomes unreliable when the probable error in measurement becomes comparable with the thickness of the 1DD-layer itself. Thus the method cannot be used to detect thin (<25μm) 1DD-layers. However, with the improved (post-HBL) resolution now available, once can spot additional clues in the edge topographs: for example in fig. 1(a) one can observe think dark bands in the (4150) reflection which mirror changes in the crystal edge morphology. These dark bands indicate heavy local defect densities and have been termed 'defect bands' by the authors. Three such defect bands can be seen in fig. 1(a) (arrowed) and are, notably, seen to coincide with respectively the 6H-15R and 15R-15R boundaries and near the 1DD-layer region. They clearly indicate some form of mismatch strain between the polytype layers. A slight change in edge morphology is also evident at the 6H-15R boundary and 1DD-layer region, and could indicate a correlation bet[ween changes in growth condition and of polytype. While these clues are useful indicators of a polytype boundary, Fisher and Barnes (1990) previously emphasized that this is not always necessarily the case. Indeed in fig. 1(a), the 1DD-6H boundary appears to be an exception in that it is not flagged by a defect band or change in edge morphology.

We now discuss cases where the 1DD-layers are too thin for unambiguous assignment 'by absence' alone. Figure 2 shows such a case, and here one must make use of the additional clues resulting from the improved edge-topography resolution. The crystal in question appears at first sight to be a singe (6H) polytype. Now it is a rule that, apart from special or systematic absences, all polytypes and 1DD-layers will be simultaneously visible with (*hk 0*) reflections since, when $l = 0$, the *d*-spacings become independent of the *c*-parameter and therefore independent of polytype. This is the case with the (4150) 'central' reflection (fig. 2(a)), and one notes that two thin defect bands can also be discerned and these are therefore earmarked as possible layer boundaries.

However (hk, $l \neq 0$) reflections from a truly 1D-disordered layer are not possible since the c-spacing would not be defined. So when an enlargement of an reflection reveals fine (<25μm) clear bands (e.g. fig 2(b)), one suspects they might be 'absences' due to 1DD- or LPP- (long period polytype) layers. Closer inspection confirms that both bands are indeed at the same sites as the defect bands (fig. 2(a)). Although assignment of 1DD/LPP layers now seems very plausible, it could conceivably be challenged on the grounds that the clear bands might be the result of zero contrast from perfectly crystalline 6H-layers rather than of missing LPP/1DD reflections. Such an explanation seems very improbable, particularly in view of the defect bands observed at the same sites. However, in this case there is yet further evidence, of a very convincing nature, to support the LPP/1DD-layer hypothesis in the case of the lower (slightly thicker) clear band. An over-exposed enlargement of a region between the main reflections (fig 2(c)) shows a thin faint repeating band corresponding to a long-period polytype (LPP) of either 152H or 456R. The thickness of these reflections (12μm) appears to be the same as the thickness of the main clear band but, more not ably, the length of the reflection is also correct. Because the lower region of the 6H polytype changes in size, one can simply project down the length of the LPP-layer (indicated in fig. 2(c)) until it matches that of the local dimensions of the crystal: this occurs precisely at the same site as the clear band. The overall evidence then is quite conclusive that a fine (12μm) heavily defective long-period polytype layer exists at the junction between the broad and narrower segments of the SiC crystal, as illustrated in the model (fig. 2(d)). The case of the second (narrower) band is considered below with that of the crystal shown in fig. 3.

With a fine LPP-layer one can search, as in the previous example, for confirmation by way of closely spaced fine reflections associated with the LPP-layer. However, in the case of true 1D-disorder, there will be *no* discrete reflections: rather the corresponding intensity will be spread out along the diffraction rows. But if we are dealing with thin layers, such streaking will be very weak and often undetectable. This was the case with the narrower of the two clear bands in fig. 2(b). One suspects it is an extremely thin (5μm) 1DD-layer but, since the associated streaking is barely, if at all, visible, the assignment carries an element of doubt. A similar case is provided by the crystal in fig.3 except, in addition, here one is also dealing with a thin (147μm) crystal. The clear (absent) band in this case is 30μm thick (fig 3(b)). An overexposed enlargement of a region between 6-H reflections (fig 3 (c)) again reveals fine LPP-layer repeats corresponding this time to 42H or 126R, in addition to an harmonic reflection from the 6H-polytype. But the repeating LPP-reflection is only 15μm thick and therefore cannot account, on its own, for the full thickness (30μm) of the clear band. The edge-topographs (fig. 3 (c)) do however display some very feint streaking with a width corresponding to the length of the clear band. The assignment here is that there is a 15μm LPP-layer immediately adjacent to a 15μm 1DD-layer, both layers being sandwiched together between 6H polytypes (fig. 3(d)). Clearly the evidence for very thin 1DD-layers can never be so overwhelming as for LPP-layers, though one should note that nevertheless there have been many observations of their occurrence during the course of this study.

In conclusion we note that fine (<25μm) LPP/1DD-layers are a common feature in silicon carbide. High-defect-density bands are usually found at the sites of these layers as well as at boundaries between polytypes. This suggests that while a sharp (syntactic) transition between polytypes can be achieved with or without inter-polytypic strain, a fine (<25μm) defective LPP- or 1DD-layer can act as a transition region between lower-period polytypes into which any mismatch strain is confined. This feature appears to be a special case of more general observation, noted previously by Fisher and Barnes (1990), that LPP/1DD-regions are *always* found to be sandwiched between *lower*-period polytypes rather than in the reverse configuration. The previous observations were made on the basis of medium (25-100μm) and thick (>100μm) layers. It is noteworthy that the 'sandwich rule' remains intact even down to the finest layers (5μm) that we can observe with the improved resolution of synchrotron edge-topography. However, it appears that the role of these fine LPP/1DD-layers with high defect densities, is quite different from that of the thicker, relatively defect-free, 1DD/LPP-regions observed previously. Together these topographic features should be able to provide us with a wealth of new information on the nature of polytypism and the mode of formation of polytypes in silicon carbide.

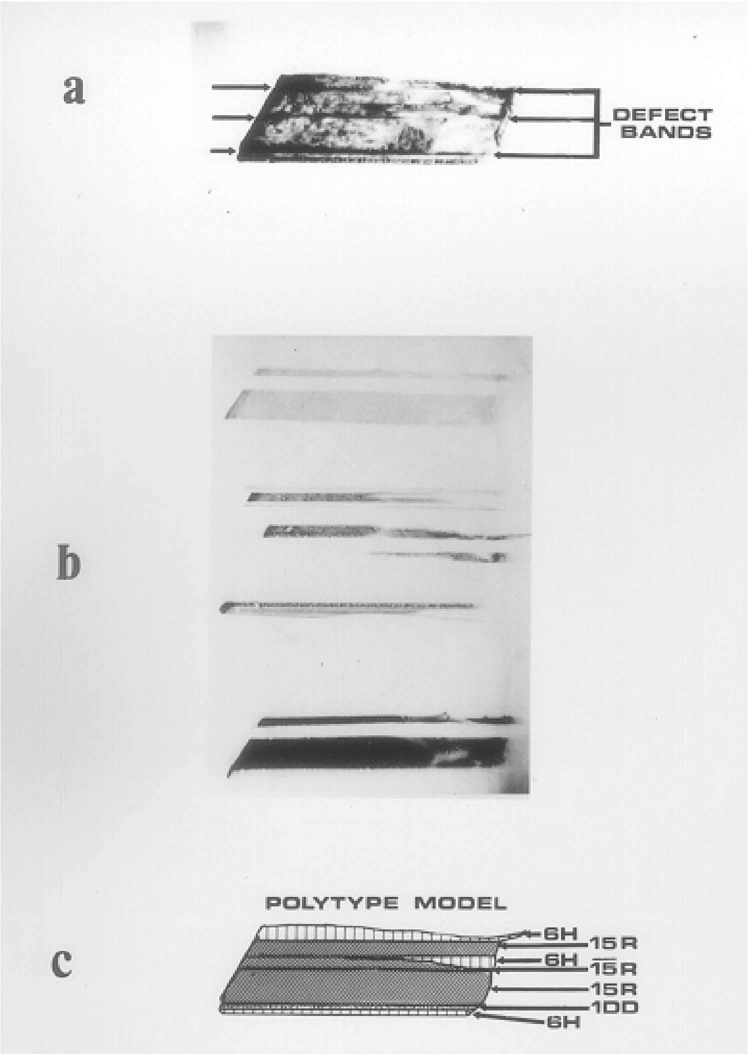

Fig. 1 Enlargements from a white-radiation synchrotron edge topograph of a complex multipolytypic silicon carbide single crystal with dimensions 6.20 x 4.84 mm and total thickness 1350μm as evident in (c). The effective wavelengths are 0.78 Å (a) and 1.53 Å (b) in the region of the displayed images.

(a) A $52\bar{7}0$ *central* reflection in which three (arrowed) defect bands are clearly visible.

(b) Over-exposed topographs for part of the $31\bar{4}l$ row where the component polytypes are well dispersed spatially.

(c) A model, to scale, of the polytypic content showing seven separate regions including a thick ~250 μm one dimensionally disordered (1DD) layer.

This topograph of sample J67 was taken after the High Brightness Lattice upgrade of the Daresbury Synchrotron and has been classified as an “asymmetric sandwich”.

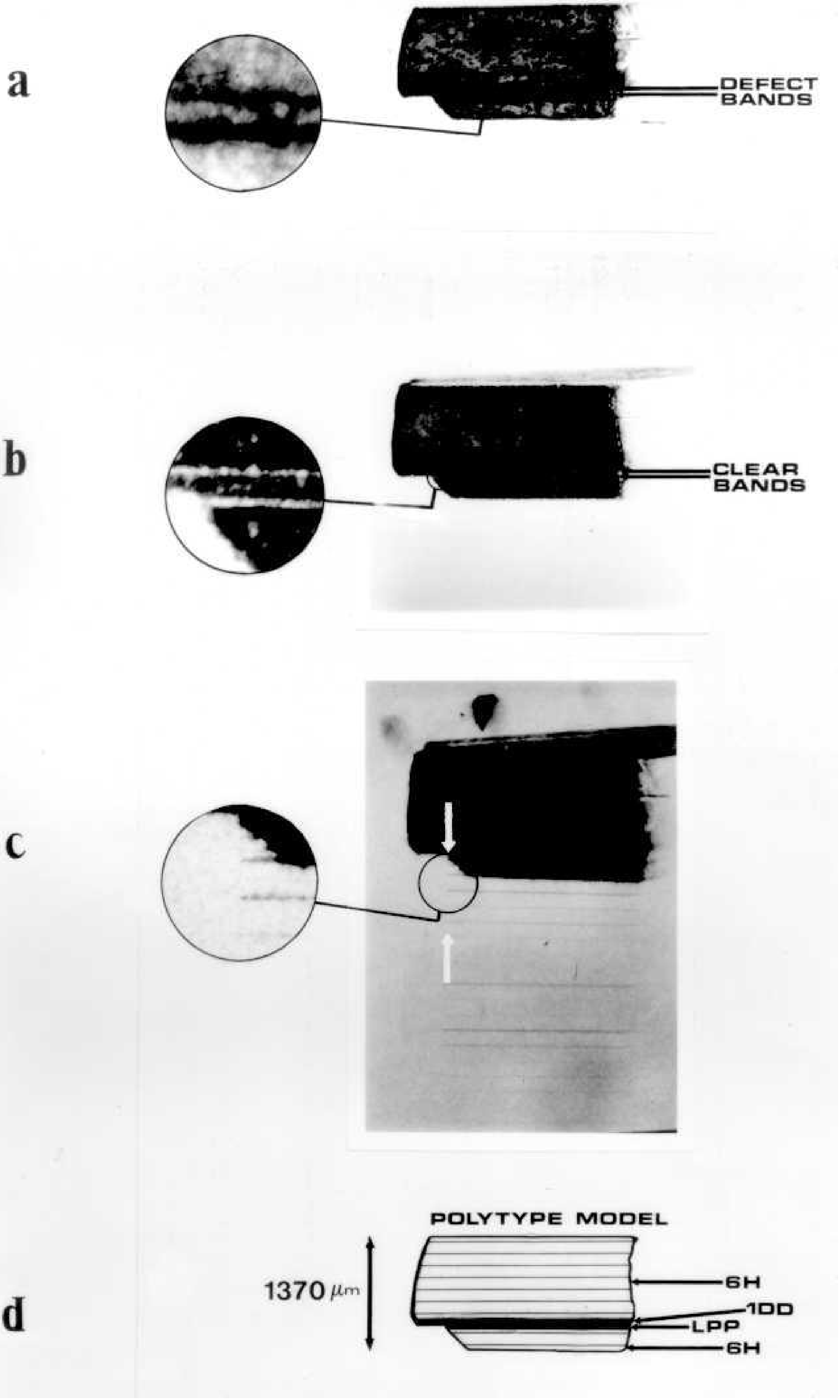
a
DEFECT BANDS
b
CLEAR BANDS
c
d
POLYTYPE MODEL
1370 µm
6H
10D
LPP
6H

Fig. 2 *(previous page)* **An idealized sandwich configuration in which long period/disordered layers are clearly seen sandwiched between a shorter period polytype. Enlargements from an edge topograph of a predominantly 6H polytype SiC crystal J26 with dimensions 4.21 x 4.05 mm and total thickness 1370µm. A new long period polytype LPP (152H/465R), previously unseen, has been identified and the LPP repeat measured from the topographic plate.**

(a) A $\{52\bar{7}0\}$ $l = 0$ reflection which provides finite contrast for all polytypes and reveals in this instance two regions of higher diffraction contrast termed defect density bands. These are shown magnified in the blow up of the circular region as would be observed under an optical microscope (magnification 167x actual size).

(b) A $\{31\bar{4}2\}$ $l \neq 0$ reflection reveals two clear absence bands which are believed to correspond to fine one-dimensionally disordered (1DD) or long-period polytype (LPP) layers. Again a magnified view is shown to the left of the topograph with clear indication from the morphology showing their location along the crystal edge in relation to the main 6H polytype.

(c) An overexposed region close to a main $\{31\bar{4}4\}$ 6H reflection showing fine (12µm) closely spaced reflections from measurements corresponding to a 152H/456R long period polytype (LPP) previously unreported (Barnes, Kelly & Fisher 1991). These are visible in the blow up and correspond to the lower of the regions indicated in (b).

(d) A model to scale of the polytypic content indicating a fine ~ 5µm 1DD layer, termed an American club sandwich 6H + 1DD + 6H + LPP + 6H.

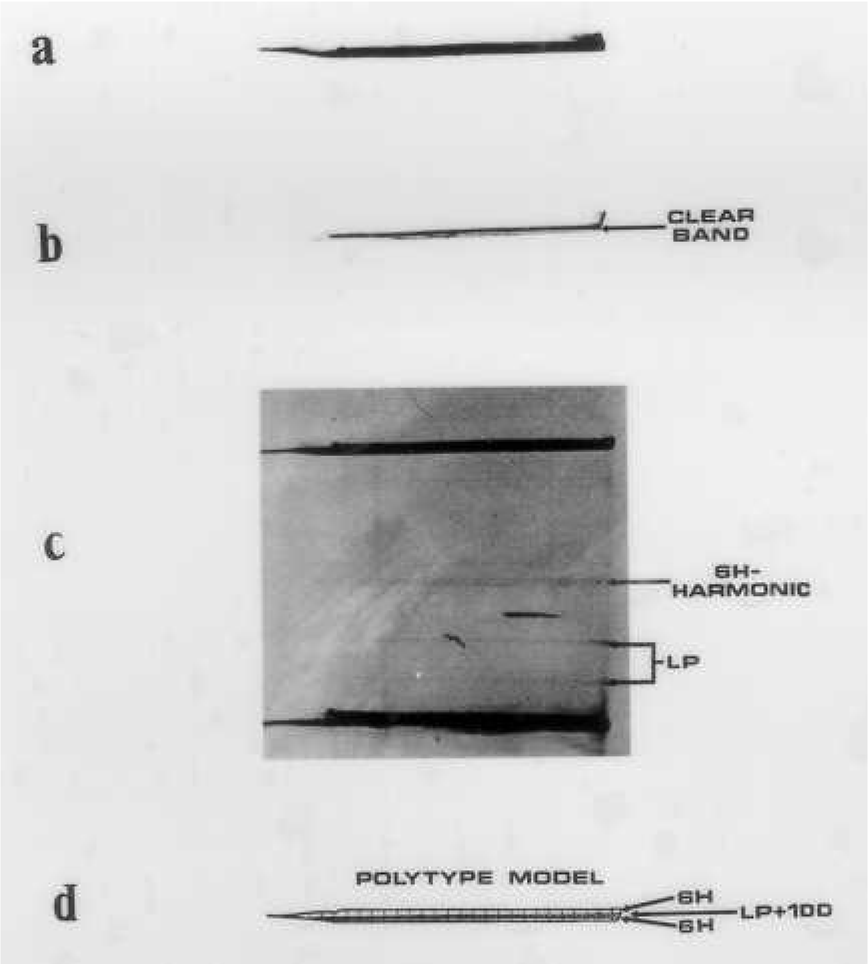

Fig. 3 Enlargements from an edge topograph of a thin (147µm) crystal J64 termed a doubly filled sandwich containing the LPP 42H previously reported by Kuo Chang-Lin (1965).

(a) A $\{41\bar{5}0\}$ $l = 0$ reflection from which the total crystal thickness may be determined.

(b) A $\{31\bar{4}2\}$ $l \neq 0$ reflection reveals a 30µm clear band due to the absence of reflection from the surrounding 6H polytype and indicates a region with either a longer or at least different unit cell c repeat or that is disordered in this direction. This is more clearly seen in (e).

(c) An overexposed region between the 6H reflections on the $\{31\bar{4}l\}$ row showing the fine LPP repeats and a 6H harmonic reflection. The LPP repeat has been measured with a thickness of 15µm.

(d) A model, to scale, of the polytypic content in which the 30µm clear band has been assigned a ~15µm 42H/126R and ~15µm one dimensionally disordered layer.

(e) Inset circled magnification of the 1DD layer described in (b).