Twin morphology: 2. Measurements of the enhancement in growth due to re-entrant corners

David M. Sadler, Marion Barber, Gillian Lark and Mary J. Hill
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

(Received 9 May 1985; revised 14 August 1985)

The morphology of double crystals and of 110 twins has been systematically investigated for a range of low molecular weights and crystallization temperatures of polyethylene. Twins with $\{110\}$ faces only (concave), those which also have (100) faces (convex), and several intermediate types have been observed. Analysis of the morphologies is given in terms of growth rates on the usual crystallographic faces and on several 'serrated' faces. The latter are not close packed and involve re-entrant corners (e.g. faces whose overall orientation is approximately along (010)). 'Enhancement' values are deduced, i.e. ratios of growth rates on serrated faces to rates on $\{110\}$. These are generally in the range 1.2–2 in spite of theoretical predictions from nucleation theories of about 10^3 or more. In the limit of low molecular weight and temperature, enhancements of 20 or greater are seen. A comparison with crystallization from long chain paraffins is included. The results are consistent with enhancement decreasing as temperature increases as a result of a surface melting phenomenon as proposed recently. Some additional effects probably due to the stereochemistry of the attachment process are also noted and discussed.

(Keywords: polyethylene; crystallization; twin crystals; re-entrant corners; growth enhancement; rough surface growth)

INTRODUCTION

The observation of enhanced rates of growth due to re-entrant corners of twins is a direct experimental consequence of a nucleation mechanism of crystal growth[1,2]. A permanent source of steps crossing the growth face obviates the need to nucleate new layers in a similar way to the well known case of growth by screw dislocation[3]. Twins have been observed to enhance crystallization for both paraffins[4,5] and polyethylene (PE)[6,7]. The implications for growth mechanisms have been recognized (e.g. refs. 4 and 5, Lotz and Wittman, personal communication). There has also been a discussion of addition of chain folded crystals to extended chain substrate with corner sites[8,9].

Part 1 of the present work, summarized below, was concerned with several types of information which could be extracted from the morphology of polyethylene twins. In particular, it was noted that substantial enhancement effects are probably restricted to low molecular weight (M) and crystallization temperature (T_c). These questions now have a particular importance because of the proposal that surface nucleation is not generally the origin of chain folding in polymer crystals[10–12].

A short summary of observations cited in Part 1[10] is as follows.

(1) From information available in the literature, substantially enhanced growth at re-entrant corners is found only at low T_c, e.g. 20°C (with low M, see below).

(2) The existence of enhancement along all of a (110) face implies that there is no mosaic block structure or other impediment to spreading of layers along faces. This is relevant to whether the growth is in Regimes I or II (see below).

(3) The interpretation of the enhanced rates is complicated by the fact that for a true twin the re-entrant corner site is a 'special' site (see also below). In addition, twins with large aspect ratios no longer have $\{110\}$ faces adjacent to the re-entrant corner, but have 'convex' ends with (100) faces. A preliminary analysis in Part 1 suggested a link between the nature of the corner site at the twin boundary and the existence of convex twins.

(4) 110 twins with (100) faces enable the straightness of the (100) faces to be examined more critically than otherwise: at moderate T_c (about 80°C) the (100) are as straight as the $\{110\}$.

(5) 110 twins with (100) faces also enable relative rates of crystallization on $\{110\}$ and (100) to be observed at higher ratios of growth rates than is possible for untwinned crystals.

(6) When some conditions are fulfilled (e.g. when 'special' site effects such as at corners are absent) it is possible to discuss a scheme of 'reduced growth rate' (i.e. rates for equivalent supercooling) for the two faces for a wide range of T_c and M. These conditions should apply to Regime II and the rough growth regime (see below). A schematic plot of rates on $\{110\}$ and (100) against T_c was given, showing in both cases a substantial decrease as T_c is decreased. These observations were all interpreted in terms of a trend towards higher equilibrium roughness and lower nucleation barriers as T_c is increased.

This paper sets out to clarify the situation for enhanced growth at corners: is the effect indeed confined to low T_c? Can any more information be obtained on what controls the incidence of this effect? Is the effect of re-entrant corners at a twin boundary different from other corners, and what is the origin of the convex twins? The experi-

0032-3861/86/010025-09$03.00

ments consisted of morphological examination for a range of T_c and M in order to establish trends empirically.

By using the full range of molecular weights, from the usual high values (e.g. 100 000) down to paraffins (e.g. C_{100}) it is possible to cover a very wide range of T_c even using only one solvent (xylene in our case). For any one M value, however, the range of T_c is limited by the very marked supercooling dependence of the growth rate. Hence it is not practicable to separate in a definite way the effects of M, T_c, and supercooling ΔT. For brevity, trends are sometimes quoted in terms of T_c, though the other two quantities may well be involved.

The observations can be considered in two parts. Firstly, double crystals involve re-entrant corners which should be equivalent to others which occur during growth (see below) without the complicating issue of the re-entrant corner also being at a twin boundary. Secondly, a considerable section of this paper is devoted to the origin of convex twins and of twins intermediate between the concave and convex type. Both of the sections can be used to derive estimates of growth rates on {110}, (100), on three types of serrated 'faces', and at the twin re-entrant corner. Some of the results are probably related to specific stereochemical effects on the growth rates. Other results concern the rates on serrated faces relative to ones which are nominally, at least, 'facets' (see below).

The main intention of this paper is to deduce the effects of serrations (re-entrant corners) on the growth, using simple geometrical arguments. To do this no assumptions are necessary about the theory of the crystallization process, though we do make use of the terminology used in the well established theories of crystallization of non-polymers (see the next section).

The results of our analysis are, however, very relevant to theories of polymer crystallization, since the hallmark of 'nucleation' theories is that enhancement of rates due to serrations on the growth face should be very large indeed.

GROWTH REGIMES AND NOMENCLATURE

The theories of crystallization for non-polymers, their application to polymers, and their relation to existing theories for polymer crystallization, have all been discussed elsewhere[10–12]. For non-polymers it is now clear both theoretically[13] and experimentally[14] that, as suggested originally by Burton and Cabrera[15], a two dimensional melting process can occur on the crystal surfaces, and that this can happen even when the crystal is not superheated. Above a transition temperature T_R the crystal surface is *rough* and growth is '*continuous*', i.e. without nucleation, in the same way as for condensation in an (anisotropic) liquid. Growth rates are expected to be linear with ΔT ($\Delta T = T_m^\circ - T_c$ where T_m° is the melting or dissolution temperature of the infinite crystal), just as is the rate of condensation on to a liquid droplet.

At low T_c however the surface relates more closely to the crystal lattice and large (macroscopic) crystal surfaces at equilibrium with their environment follow (close packed) crystallographic directions to the precision of one lattice spacing (they are then '*facets*'). Departures from faceting must involve surface steps which have a finite free energy per length. Because of this latter fact the density of steps crossing a surface is strictly zero for an 'infinite' surface in equilibrium. If a supercooling is now applied under these conditions, growth is only possible either if some defect acts as a source of steps or there is *nucleation*. The growth rate then depends on $\exp(-K_g/T\Delta T)$, where the exponent is related to the (relatively high) free energy barrier for the formation of a two dimensional nucleus whose height is one lattice spacing greater than the rest of the surface. Once a nucleus has passed its critical size the probability of it being removed is generally small. The remaining process of growth, subsequent to nucleation, we term *completion*.

A polygonal (as opposed to a rounded) crystal habit implies that the need for nucleation may be impeding growth at least to some extent: growth on all faces with orientations other than these occurs by completion alone and is therefore faster. By contrast, rounded morphologies indicate that surface orientations which require many steps do not give significantly faster growth than those that do not. These statements do not depend on a detailed analysis of the particular type of curvature present.

For polymers, strictly, 'facets' or 'nucleation' cannot be expected on the growth faces, because they are limited in width to only 100 Å or so in the direction along the lamellar normals. What is more, growth is usually under conditions even further from equilibrium than for most other crystals. It has been proposed nevertheless that there is a change from low to high step density as T_c is increased[11].

For those cases when crystal thickness varies with ΔT, the growth law universally observed for polymers is the exponential one characteristic of nucleation. It has now been proposed that this is, in many cases at least, coincidental. It is proposed that the form of the dependence of G on ΔT is the consequence of an entropic barrier to growth related to attachment of long chain molecules[11,12] and that this barrier increases with crystal thickness. In parenthesis, it may be remarked that the exponential dependence of G on ΔT does not apply when the lamellar thickness is, at least for some T_c, constrained to be constant, and is not a strong function of ΔT. The growth rates for oligomers of poly(ethylene oxide) are, in these circumstances, linear with ΔT, in accord with a rough surface (no nucleation)[16].

In this paper we use the terms 'nucleation' and 'completion' without reference to any very specific model. By contrast most previous work on crystallization of polymers has used the model of complete stems (chain sequences crossing lamellae) attaching and detaching as single units. In the case of the Regime III analysis[17] 'completion' and 'nucleation' are used to denote, respectively, the *attachment* of a stem either with, or without, a lateral neighbour on the growth face. This is not the terminology used in this paper. It should also be mentioned that Regime III is different from the rough surface growth discussed here, for several reasons.

The morphological criterion given above suggests that polymer crystals with straight edges have a finite nucleation barrier, either instead of or in addition to the entropic barrier mentioned above. This is the situation considered in this paper. It has been recognized in general[18] and for polymers in particular[19,20] that for 'nucleation' there are two distinguishable regimes. If, on average, the steps generated by a nucleation event reach the ends of the faces before a second nucleation occurs the growth is in 'Regime I'. Nucleation is then the sole rate controlling process. If, on the other hand, more than two steps are normally present, the growth rate depends both on the nucleation rate, *i*, and the completion rate, *g* (Regime II). Regime I can be expected only if net addition to corner sites is several orders of magnitude faster than at smooth sites, and should result in growth increasing with the lateral size *L* of the crystal.

EXPERIMENTAL DETAILS

Several low molecular weight polyethylene fractions (M_w 2500, M_n 2300, M_w5300, M_n 1900; M_w 9000, M_n5000; M_w 15000, M_n 11000) were dissolved in xylene (usually at 0.01% weight by volume), and cooled in test tubes 10 mm in diameter to 23°C. They were then heated to temperatures in the range 95°C–99°C and transferred to temperature controlled baths at temperatures in the range 23°C–90°C. Crystals were dried on to carbon films and examined in a Philips EM301 microscope. Some were subjected to particular decoration treatments for reasons irrelevant to this paper, see Figure legends.

DOUBLE CRYSTALS (SIAMESE TWINS)

These are not twins in the sense that only one orientation of crystal lattice is present, but have features in common with twins. Presumably the crystals touch during growth, come into crystallographic register, and continue to grow so as to give the appearance of two lozenges merged at their apices (*Figure 1a*). The re-entrant corner formed at the boundary between the two parts should be identical in environment to a step across the growth face of a (faceted) crystal. We have observed crystals (*Figure 1a*) which are clearly doubled as in the original reports[23]. However, at low M and T_c they are not observed. Instead we observe crystals as in *Figure 1b*, and *Figure 1c*, which clearly have a relation to those in *1a*, but where the re-entrant corner has enhanced the rate of growth substantially. Strikingly, in *Figure 1b* and *Figure 1c*, the enhancement has not occurred on one side because of a spiral. A re-entrant corner then no longer exists, as indicated in *Figure 2a*. This diagram is adapted from Figure 11 of Khoury[5] who has discussed this phenomenon.

Fortuitously, the crystals in *Figure 1c* have been 'decorated' by some unknown substance (oil impurity presumably). From this we can see that the two parts have, apart from the 'grown-out' section, grown in the conventional manner with 4 {110} sectors.

31 cases of 'growing out' have been recorded, all for $M=2500$, $T_c > 23°C$ and for $M=5000$, the lower T_cs. For one of these a completely convex shape was not obtained, though even in this crystal the 'enhancement' was found to be relatively large (see below). 32 cases of non-grown out double crystals have been seen for other conditions. These observations are consistent with extensive work on seeding of crystals, where complete 'growing out' only occurred in the presence of low molecular weight species (D. J. Blundell, personal communication).

There is the possibility that the double crystals which have not grown out do not do so for want of polymer from solution. This seems implausible since (see the following analysis) they have grown to at least some extent *as* double crystals, and differences in growth rates on different faces should have been made evident. In addition there would, in this case, be no obvious reason for the correlation between increased enhancement and low T_c.

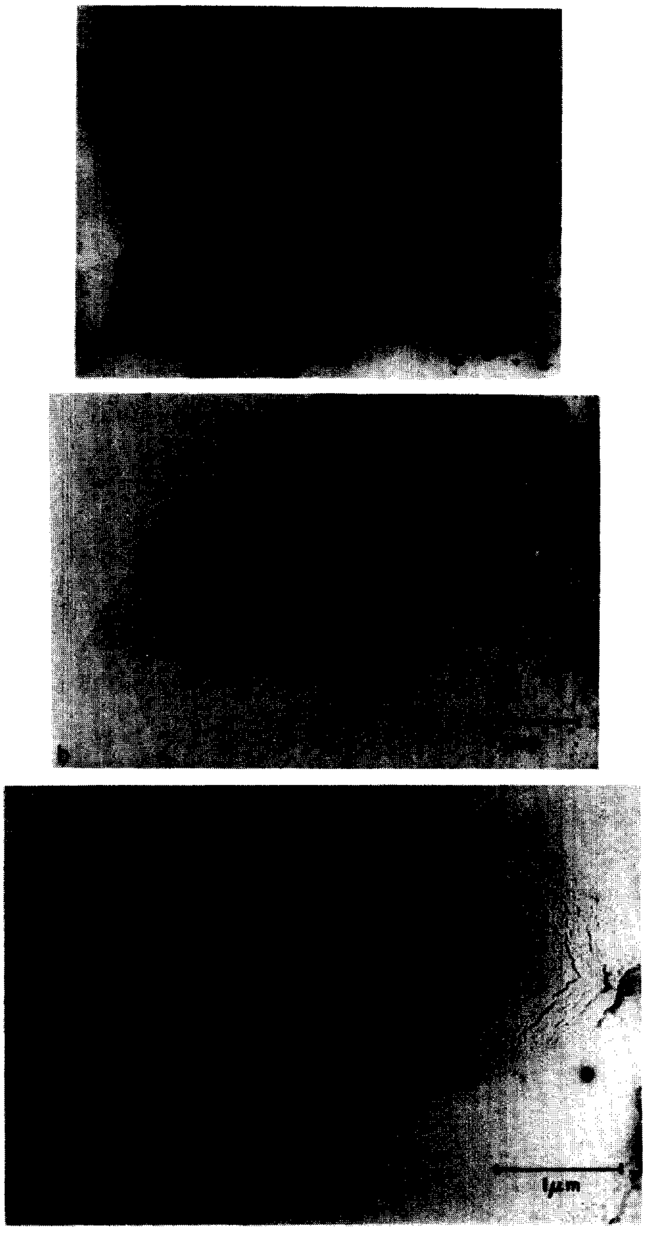


Figure 1 Electron micrographs (no deliberate shadowing or decoration) of double crystals: (a) $M=5000$ $T_c=43.5°C$; (b) and (c) $M=2500$, $T_c=23°C$

More information can be extracted on the basis of the following analysis. *Figure 2b* and *2c* show that the morphological observations can be used to derive limits for the ratio of growth rates on to {110} faces (G_{110}) and on to (serrated) faces whose average direction is along (010) (G_{010}). The schematic diagrams in *Figures 2b* and *2c* show a projection of a three dimensional structure. However, even if the steps across the growth face are not straight[11] they will be sufficiently short to be adequately represented, for our present purposes, in this simplified fashion. *Figure 2b* shows that if the convex corner pointing along ⟨010⟩ is to be retained, G_{010} must exceed G_{110} by a factor of sec α (α is indicated in *Figure 2b*). The dotted line shows to where growth on a wide (010) 'face' might have reached. If, instead, $G_{010} < G_{110}$ sec α then the apex would have been truncated. (The value of sec α is 1.2). This follows from the usual rule for growth of convex-shaped crystals: only the slower growing face is observed. The complementary situation is shown in *Figure 2c*. The

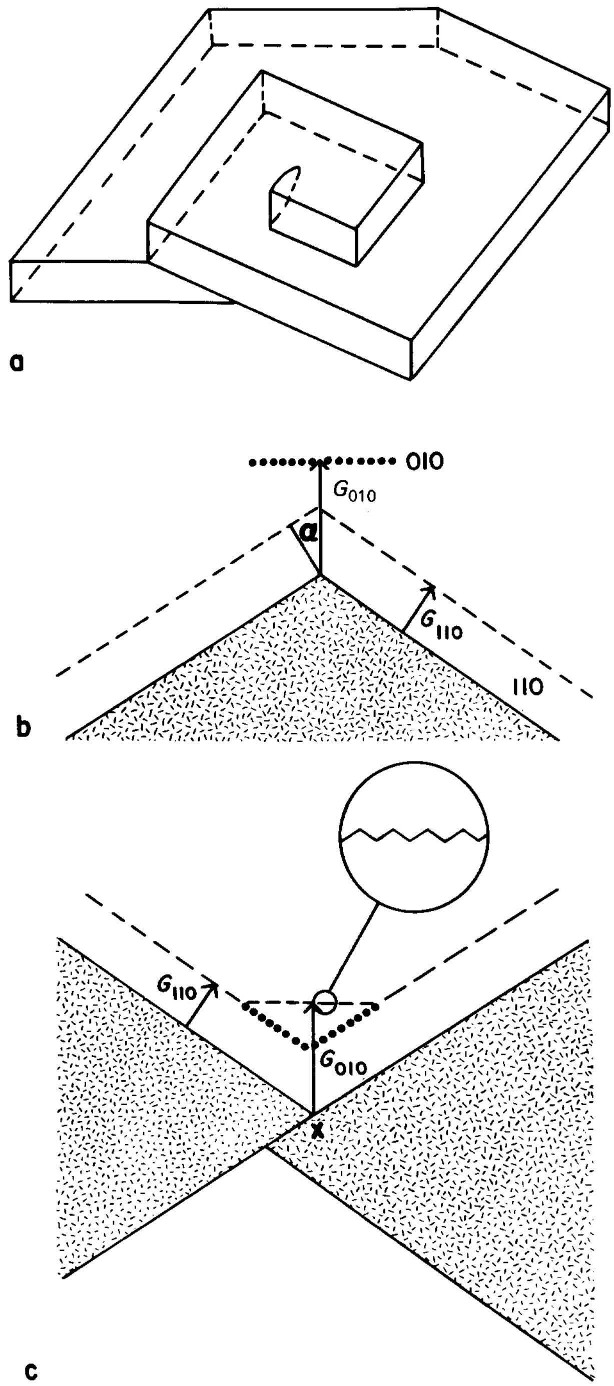


Figure 2 (a) Diagram adapted from Figure 11 of ref. 5, showing how a spiral has no re-entrant corner (cf. the upper edges of crystals in *Figures 1b* and *c*). (b) To show how G_{010} must be greater than G_{110} sec α for the convex corner pointing along ⟨010⟩ to be retained. (c) To illustrate the type of growth at the re-entrant corner of a double crystal. Solid lines: crystal outlines when crystals met; broken lines: result of subsequent {110} growth; dotted line: result of growth on (010). The inset illustrates very schematically the fact that the (010) face would be serrated in some way

solid lines refer to the outlines of the two crystals just at the instant when they come into lattice register. Only if G_{010} does not exceed G_{110} sec α will the re-entrant corner at X be the same shape after subsequent growth (shown by the dotted line). Hence only in the special case where $G_{010} = G_{110}$ sec α will both the convex and concave corners be retained during growth of the double crystal. Hence under conditions where the habit is normally polygonal we would expect to see some 'filling in' as in *Figure 2c*, and indeed this can be seen both in *Figure 1a* and in the previous publication[23]. The inset in *Figure 2c* indicates a serration which is regular on a molecular scale (i.e. a row of re-entrant corners). There is no reason to expect that the regular serration, or the overall orientation parallel to (010), should be retained, and in fact the observations show a curved irregular outline for the 'filling in' crystal portion.

With the use of dimensions as indicated in *Figure 2c*, which can be estimated from the micrographs, ratios of G_{010} to G_{110} were made. *Table 1* includes this information. The only case where growing out was not complete for $M = 2500$ and $T_c = 23°C$ gives a ratio of 20. In this particular case very little growth occurred on the {110} faces not adjoining the re-entrant corner after contact between the parent crystals. For other double crystals under these conditions only limits to the ratio were obtained (e.g. > 5 or > 12). For other conditions the ratio is less, typically no more than 2.

CATEGORIES OF 110 TWINS (OBSERVATIONS)

A large number of twins have been observed, and before interpreting their shapes the conditions where they occur will be described. The concave twins with only {110} faces and high aspect ratios (*Figure 3a*) are always observed at low T_c and low M as inferred previously[10]. One important qualification of this statement is that concave twins are frequently seen when a growth spiral occurs on the twin boundary (*Figure 3b*). Since in these cases no re-entrant corner is present as illustrated in (*Figure 2a*) the crystals should behave simply as 'double lozenges'. The fairly large but variable aspect ratios presumably occur because of enhanced growth prior to the creation of the spiral. As one would expect, concave twins with spirals are observed for all conditions (see below). A referee has pointed out the curious feature that the spiral in *Figure 3b* is not along the centre line of the twin. This may be because the twin plane does not follow the ⟨110⟩ direction accurately (see also *Figure 3a*). The twin plane direction could be studied with the use of a suitable decoration technique (see note in proof).

The convex twins, with growth enhanced along (100) faces (*Figure 3c*) occur for M higher than a moderately 'high' value of about 5000. The convex 110 twins with aspect ratios around unity are the ones which have been observed at the more typical 'high' molecular weight (*ca.* 50000) and high T_c (*ca.* 85°C)[24]. For comparison *Figure 3d* (courtesy of S. Organ) shows a 110 twin grown under conditions where the nominally (100) faces have become rounded ($T_c = 110°C$). There is no significant enhancement effect.

We can now present a range of interesting morphologies intermediate between *Figures 3a* and *3c*. (A hypothetical crystal of this type has been discussed[10].) These are shown in *Figure 4*. On occasion the crystals are convex apart from a piece missing from the tip (*Figures 4a, 4b*). J. C. Wittman has noted morphologies of this kind (personal communication). In other situations the tip is serrated (*Figure 4d*) or straight and approximately parallel to (010). *Figure 5* summarizes the information concerning conditions where the various morphologies have been observed.

Table 1 Summary of the ratios of growth rates along the twin plane direction *u* which have been extracted from the micrographs. If the growth face has a crystallographic index, G has the corresponding subscript (G_{110}, G_{010} and G_{100}). If it does not, the angle with the (100) face is given, e.g. $G(33)$. $G(33)$ and G_{010} must be serrated faces (see text and *Figures 2* and *6*). The prime on G'_{100} indicates that the consequence of G_{100} along *u*. $G'_{100}=G_{100}/\cos\gamma=1.2G_{100}$. As explained in ref. 10, higher ratios of G_{100}/G_{110} can be measured on twins than otherwise. G_n is the growth of the twin plane exit re-entrant corner '*n*' along *u*. It can readily be used to calculate $G(60)$ corresponding to faces at an angle β to {110} (another serrated face). The number in brackets indicates the number of individual results where there are more than one

		Crystals used for measurement			
		Convex	Double	Intermediate	Concave
Mol. wt.	T_c(°C)	G'_{100}/G_{110}	G_{010}/G_{110}	$G(33)/G_{110}$	G_n/G_{110}
2300	23		$\geqslant 6$, $\geqslant 8.3$		
			$\geqslant 3.5$, $\geqslant 5.5$		6, 6.9
			$\geqslant 19$, $\simeq 20$		
	39				3.4
	43.5				5.4
5000	23		1.2	2.9 (5)	
	33			2.4	
	43.5			2.4 (5)	
	50		2.2	2.6 (7)	
	60	3.1	1.5	2.8 (3)	
	63.5	3			
	71	3.1 (3)	1.5	2.5 (3)	
9000	51	3.5		2.7, 2.1	
	70	2.6 (2)		3.5 (2)	
15000	50	3.5, 2.8	1.4–2		
	70	3.9			

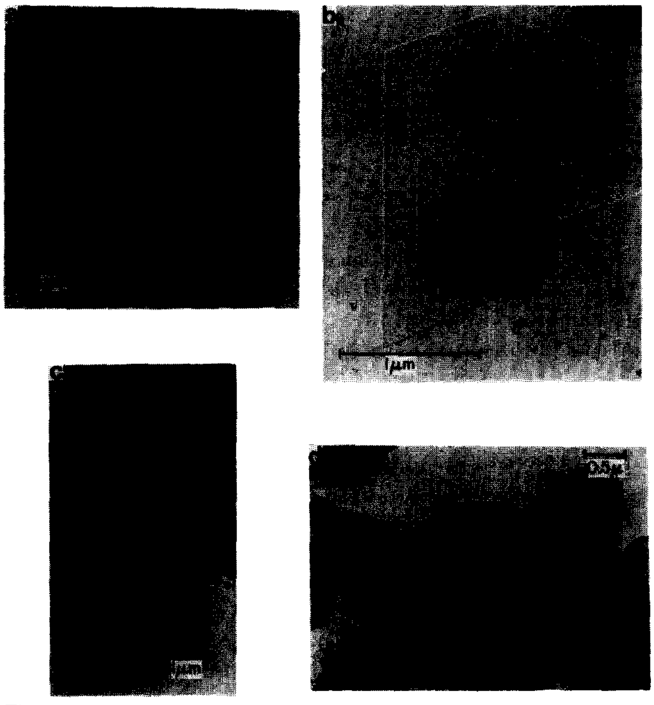


Figure 3 Characteristic types of 110 twins (electronmicrographs): (a) Concave ($M=2500$, $T_c=23$°C) decorated with evaporated hydrocarbons, courtesy of B. Pretzel, according to the method of Lotz and Wittman[31]. (b) With growth spiral and hence no re-entrant corner. (See *Figure 2a*). $M=2500$, $T_c=43.5$°C shadowed. (c) Convex ($M=15000$, $T_c=70$°C). (d) Twin grown under conditions where large curved nominally (100) faces are observed. $M=100000$, $T_c=111.8$°C, solvent Tetradecanol. Crystal Pt/Pd shadowed. (Courtesy of S. Organ)

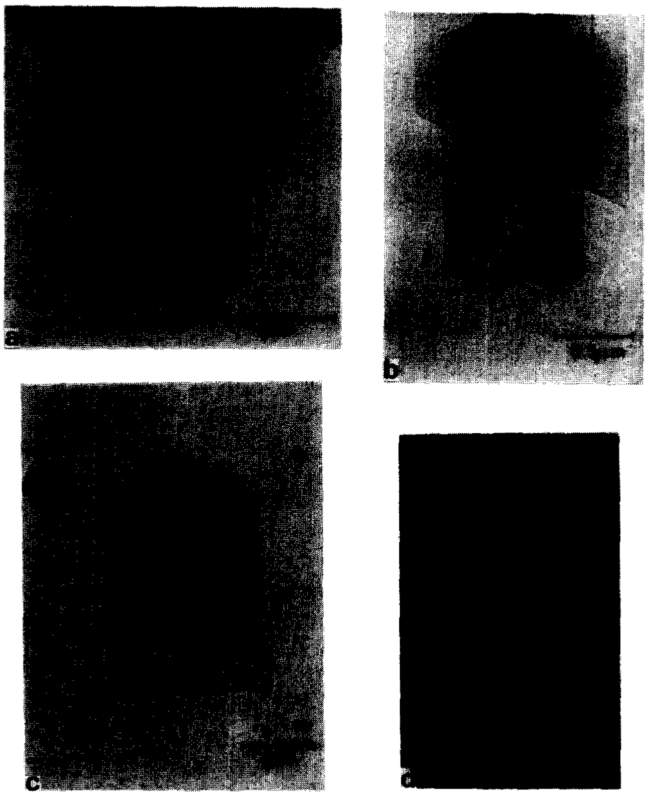
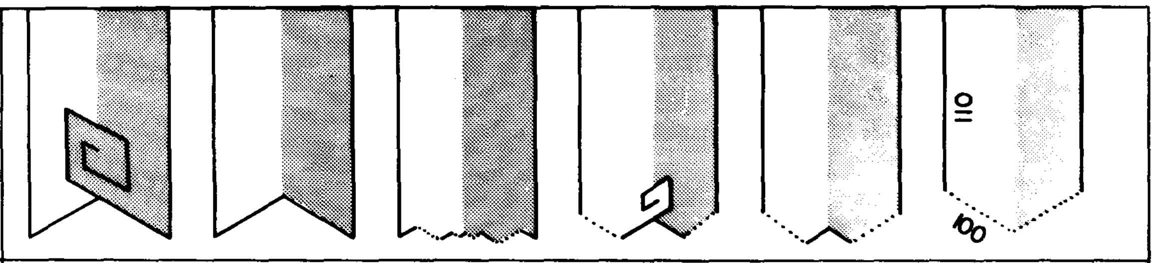


Figure 4 Electronmicrographs of 110 twins intermediate between concave and convex. (a) $M=5000$, $T_c=70$°C and (b) $M=9000$, $T_c=71$°C with both {110} and (100) faces adjoining the twin boundary exit. For (a) the junction between {110} faces is not sharp. (c) $M=2500$, $T_c=43.5$°C and (d) $M=5000$, $T_c=50$°C typical of crystals with faces approximately at right angles to the twin boundary. These faces can be fairly straight or irregular to varying degrees. *Figures 4b* and *4c* Pt/Pd shadowed

ANALYSIS OF THE CONVEX AND CONCAVE TWIN SHAPES

On the basis of the section on double crystals, one would have anticipated an enhancement in the direction of the twin plane such that the aspect ratio of the concave twins increases with decreasing $T_c(M)$. This is indeed the general trend which is observed (see also Part 1). However, at high T_c the twins become convex, and at intermediate T_c there are transitional types. It can be seen that the morphology is not restricted to faceted crystals, nor even to crystals



MW	Tc (°C)	No. of crystals observed						
2500	23	35	3	32				
	33	19	1	7	11			
	39	20	6	3	11			
	43.5	30	2	2	19			7
	49	6	1					5
5000	23	25	14		10		1	
	33	23	6		5		6	4
	43	29	10		8		3	8
	50	49	7	4	10		13	15
	60-63	39	4	2	2	1	7	23
	70,71	57	12		5	2	5	33
9000	33	29	29	dendritic				
	43.5	21	18	dendritic				3
	50	8	1			1	3	3
	70,71	31	6			3	7	15
	82,83	20	5					15
15000	43.5	26	4			2		20
	50	29	5			2		22
	70	12	5					7
	74.5	24	17			1		6
	87.5	29	5			1		23

Figure 5 Chart of the various morphological types and their occurrence. The shapes in columns 4–9 are schematic and simplify some of the important features (see text), e.g. the re-entrant corner in crystals shown in column 8 is not always sharp

with significant lengths of facets ('microfacets'), and, in fact, there is no reason to suppose that this is likely *a priori* (*cf.* the short preliminary discussion of convex twins in Part 1, which, implicitly at least, presupposed the existence of microfacets). Several situations can be identified where the natural interpretation is of a serrated 'face' as discussed already for *Figure 2c* (e.g. in *Figure 4c*). Again, for '{110} faces' adjoining the re-entrant corner of concave twins there is commonly a finite angle β between the face and {110} direction (indicated in *Figure 6a*). β values are in the range 0°–10°. In order to include orientations of faces which do not follow $\{hk0\}$ orientations it is convenient to introduce an additional notation for which $G(\theta)$ denotes the growth rate for a face inclined with its normal at an angle θ to the a axis ($\langle 100\rangle$). (In this notation G_{100} is $G(0)$, G_{110} is $G(66)$ and G_{010} is $G(90)$). In addition we need to consider G_n, which is the growth rate at the re-entrant corner site at the exit of a (110) twin plane at the growth face (e.g. see the bottom of *Figure 3a* and also *Figure 6a*). The most appropriate quantity for detailed analyses of morphology is a vector 'slowness'[29]. However, the present discussion is restricted to comparisons of growth rate for the same direction u, which is a vector along the (110) twin plane direction. To do this for parts of faces near the twin boundary we need only compare different values of:

$$G(\theta)/\cos\gamma \equiv G'(\theta)$$

where γ is the angle between the growth plane normal and γ for (100) faces is 33°.

G_{010} ($G(90)$) is on a face which is serrated to some degree, so that the growth rates such as that will be closely related to completion rates, e.g. along {110}, which also involve additions to re-entrant corner positions.

For twins with approximately flat irregular faces (e.g. *Figures 4c–4d*) with normals along u, one can associate a growth rate corresponding to $\theta = 33°$ ($G(33)$). Similarly, the concave twins involve faces adjoining the 'n' site which correspond to $G(60)$ (taking a typical β value of 6°).

There is a range of possibilities according to the relative magnitudes of the rates along u. If any one rate is much smaller than the others then the corresponding process will control the morphology. For example, a relatively small value of G_n will lead to concave twins, whereas a small value of G'_{100} will lead to convex ones. *Figure 6* describes this diagrammatically. The crystals are imagined to have grown for unit time, so that dimensions can be labelled according to the growth rates. The faces which would have resulted from the faster processes are indicated by dotted lines. The intermediate crystals (ii) and (iii) result when two rates are of similar magnitude. The different types are listed as follows.

Concave twins correspond to G_n limiting the growth. In this case steps which originate at the twin plane site grow along the {110} faces faster than their initiation rates at n. This generates faces which are approximately {110} but where the obliquity β indicates a series of steps (growth rate '$G(60)$').

Intermediate type (*i*) will result if $G_n \simeq G(33)$ but where both are smaller than G'_{100}. One can then visualize a

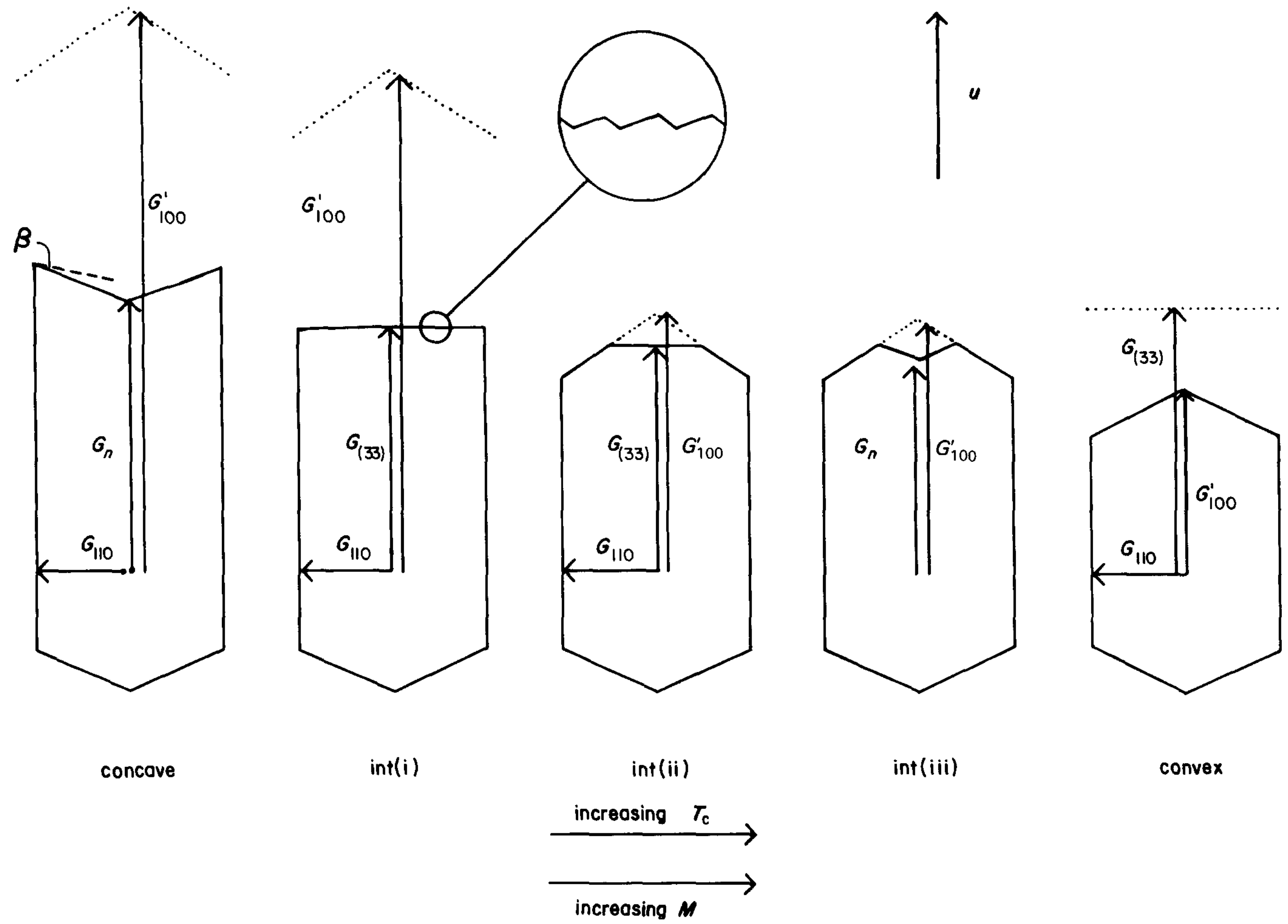


Figure 6 Schematic representation of the crystal types, with an interpretation of why they occur in terms of relative growth rates. u is the direction along the twin plane so that $G' = G/\cos\gamma$ (where γ is between u and the normal to the growth face) is the growth rate near the twin site exit along u from the rate G. The slowest growth process defines the shape which results (solid lines); the dotted lines indicate the results of some of the faster processes. The broken line in (a) shows a typical orientation which is observed, at an angle of β to the 'ideal' (110) face (solid line). Other details are discussed in the text

'cascade' of new layers on $\{110\}$ being initiated at n—a new layer starting before the previous one has had time to progress along $\{110\}$. The face which results may be serrated on a molecular scale (see inset) even though there is no reason why such serration should be regular.

Intermediate types (*ii*) *and* (*iii*) result from G'_{100} being comparable with the other rates. It is difficult experimentally to distinguish (ii) and (iii). In some cases at least a re-entrant corner appears to be sharp enough (*Figure 4b*) to suggest that G_n is slower than $G(33)$ (but *cf. Figure 4a*). In *Figure 5* candidates for both types have been included in the same column. It seems likely that only in the limit of low M and T_c is G_n systematically smaller than the other rates.

Convex twins result when G'_{100} is the slowest process.

The types of twins seen experimentally can readily be identified from *Figure 6*. As a consequence growth rates relative to G_{110} can be estimated, and the results of this will be discussed in the following sections.

GROWTH RATES ON SERRATED FACES: ENHANCEMENT

In Part 1 the relative rates of growth on the faces $\{110\}$ and (100) were discussed (both faces capable of approximating to facets, with low step densities). We are now in a position to estimate relative rates for various kinds of serrated faces (G_{010}, $G(33)$ and $G(60)$) from observations on both double crystals and 110 twins; this is of particular interest to theories of crystallization since these growth rates are closely related to completion rates (see Discussion). In some cases, only limits on the ratios of rates can be obtained, e.g. for the 'grown out' double crystals. The results are in *Table 1* as ratios of rates to G_{110} for $\{110\}$ faces with no permanent re-entrant corners. At this stage it is not known whether there is a crystal size effect on G_{110}: this is not likely to affect overall trends.

The estimates are self-consistent in that for comparable conditions $G_{010} \simeq G(33)$, these two rates being estimated independently from double crystals and 110 twins respectively. These rates correspond to rather similar serrated structures (insets in *Figures 2c* and *6*).

There is a variation of about 20% in the measured ratios of growth rates even for the same sample. Hence, for example, the values of $G(33)$ for $M = 5000$ cannot be said to change significantly with T_c, even though average measurements for a number of crystals are quoted (the number in brackets is the number of individual measurements). $M = 2500$ and $T_c = 23°C$ (two separate samples) clearly behaves differently from the other conditions: G_{010}/G_{110} is significantly higher. One would anticipate other systematic variations, but the data do no more than hint at this possibility. There are good theoretical grounds to anticipate that enhancement should decrease as ΔT increases (and a related kinetic effect has been suggested for poly(ethylene oxide)[16]). There is a precedent for enhancement to decrease as T_c increases: the loss of straight crystal faces as T_c is increased for molecular weights in the 'normal' range of $\simeq 50\,000$ has been discussed elsewhere[11]. It is quite conceivable therefore that both ΔT and T_c have effects, but that in many cases they tend to cancel out.

It is striking that only in the limit of very low M and T_c does the enhancement exceed a factor of about 2. Even then it is probably only about 20. This is in contrast to predictions of much larger values under these conditions (see discussion).

DISCUSSION OF RELATIVE GROWTH RATES

Completion at the twin site (n)

The re-entrant angle at n is distinctly more obtuse than at other corner sites so that it seems reasonable to expect the completion rate ot be correspondingly slower, which appears to be the case in the limit of low M and T_c. For high M and T_c, the morphologies of the twins suggest that completion at n is not always slower (e.g. types (ii) and (iii)). This may possibly be due to a compensating increase in growth rate because of a twin site being inherently more favourable for attachment for some reason. An interesting precedent for such a possibility has been found in poly(ethylene oxide). When a twin boundary emerges on a (120) face (where no corner is present) it is a site of preferred growth[25]. The possibility of the twin site promoting growth was mentioned in Part 1, though the preliminary explanation of convex twins given there (which was based on this effect) has now been superseded by the preceding section.

(100) growth rate

It is remarkable that G_{100}, on a nominally faceted face, can be *less* than rates of growth on serrated faces. This recalls an analogous situation at high T_c (approximately 95°C for growth from xylene solution) where PE crystals are approximately hexagonal in shape ($G_{010} \simeq G_{110}$) even though $\{110\}$ faces are straight, and '(100)' are curved (and hence have plentiful steps). It seems that in many cases at least, nucleation barriers have only a small effect on growth rates, so that 'inherent' growth rates, governed probably by stereochemical effects, can result in a face with plentiful steps growing as slowly as, if not slower than, one which is straight.

The idea of 'inherently' slow rates leads to the scheme for G_{100} and G_{110} in Part 1 (*Figure 3*) with G_{100} displaced downwards on a logarithmic scale compared with G_{110}. Another result which was attributed to the same origin is the leaf shaped morphology found for melt growth, which must be[11] a consequence of a slow growth rate along $\langle 100 \rangle$. Since under these conditions there are no suggestions of faceting, this slowness is deduced to be an 'intrinsic' effect, presumably because of the molecular details of re-entrant corner sites on (100) being less favourable for attachment than on $\{110\}$.

An analysis has been given of relative rates of growth on (100) and $\{110\}$ faces in terms of nucleation theories[30]. These theories require that nucleation is extremely slow compared with completion (i.e. that 'enhancement' at corners is very high).

The limit of low M*: crystallization of paraffins*

An important observation, which has not received much attention, is that for melt crystallization of C_{100} paraffin (high T_c) the outlines of the lozenge shaped layers[4] and of steps on much larger crystals[5] are *distinctly curved*. Hence the surface melting hypothesis is likely to apply. Furthermore, the rounding, unlike that in PE, results in approximately diamond shaped crystals. This implies that there is no 'inherently' very low rate on (100) for paraffins.

For these paraffin crystals concave rather than convex 110 twins are always seen, which implies that G_n is less than both $G(33)$ and G'_{100}. The increase of growth due to twin boundaries may therefore be specific to chain folded polymers (poly(ethylene oxide), and probably polyethylene, see above).

It may be that both these effects (growth on (100), which is inherently relatively slow, and the promotion of growth due to the twin site) have their origins in stereochemical effects, i.e. the particular molecular detail is involved. They may in fact be related to chain folding.

From the published micrographs, there is no detectable obliquity of the $\{110\}$ faces adjoining the twin site (i.e. $\beta \simeq 0$). (On the other hand, there can be a serration as in dendritic crystals due to diffusion effects[5].) This implies that the density of steps is less than for '$G(60)$' growth on the polymer crystals, though the enhancement as judged from the aspect ratios of the crystals is at least as great if not greater. This suggests that the enhancement effect of each step on $\{110\}$ faces is greater for paraffin ($M = 1402$) than for the lowest molecular weight polyethylene ($M = 2500$). The latter, in turn, showed larger enhancement effects than for the higher M (5000 and 15000). Hence the observations on paraffin crystals support the conclusion that low M, or at least the associated low T_c, is the origin of the larger enhancement effects.

Relevance of the observation to theories of crystallization

Although a number of effects have been discussed in connection with the twins, deductions concerning the influence of re-entrant corners on growth rates are both the most definite, and the most interesting from the point of view of understanding polymer crystal growth. They will be discussed here in a preliminary way only. The 'enhancement' is defined to be the ratio of growth rates on faces deduced to be serrated to that on an appropriate straight crystallographically defined face ($\{110\}$ in our case), and can be measured fairly directly as discussed above. Predictions of enhancements will involve nucleation rate i and completion rate g per stem site on the growth face (see also the Introduction). If all the surface sites on the serrated faces were of the corner type (insets in *Figures 2c* and *6*) the growth rate (measured in terms of numbers of layers) would then by given by g only. The irregularity of serrated faces is usually large enough to be apparent in the micrographs, and we anticipate that a large proportion, even if not all, of the surface sites then consist of re-entrant corner sites. Hence g should be larger than, but of a similar order of magnitude to, the measured rates on serrated faces. The rates on the crystallographically defined faces, such as $\{110\}$, will depend also on i (and sometimes the length L of the crystal growth face)[19,20]. For example in Regime II it will be $(ig/2)^{1/2}$. Hence a rough estimate of enhancements (if indeed Regime II is appropriate) would be given by $(g/i)^{1/2}$. Data for polyethylene using the previous nucleation theories[21] would give a value of about 10^3 (Regime I would give even higher values).

The observation of polygonal habits need not involve high enhancements, e.g. for the apex pointing along ⟨010⟩ to be retained, the ratio G_{010}/G_{110} need be only 1.2. Nucleation theories, however, involve enhancement values of about 10^3. The data in *Table 1* are interesting in that enhancements are much nearer unity than one would expect from the nucleation theories. This is in fact reasonable since many micrographs of polyethylene crystals, here and elsewhere, show significant irregularities in their outlines compared with the idealized geometry, which suggests that there is not a factor of 10^3 in the preference for growth at such irregularities.

These results, together with previous arguments[10], make it appear increasingly unlikely that Regime I can be observed in polyethylene. The crystal size L has never been found to increase the growth rate, as it should in Regime I (the longer the substrate the higher the probability of nucleation on it). There is the possibility that defects on the growth face would reduce the effective 'L' by making one face a composite of many smaller faces. The preceding paper[10] pointed out that the morphology of twins was not consistent with this last hypothesis. We now find that the enhancement at re-entrant corners is very much less than required for Regime I to be accessible experimentally.

The comparatively low enhancement rates imply that even in the 'faceted' regime there is a substantial degree of roughness on the growth faces so that there is a significant entropy contribution to the step free energy. One would judge that the processes which have been proposed for rough surface growth (no facets at all)[12] may also be relevant even when 'facets' are present.

The new approach involving roughness on the growth faces is not in general restricted to any particular values of enhancement, but one would expect an increase as T_c is reduced. The results are certainly not in disagreement with this; at high T_c (e.g. *Figure 3d*) curvature indicates that the enhancement is about unity; at T_c 30°C–70°C enhancement is 1.2–2, for one particular case ($M=2500$, $T_c=23$°C) it is $\gtrsim 20$, and for paraffin crystals (C_{100}) it may well be larger still. As has been discussed above, there are some ambiguities as to what are the quantities of primary importance in controlling enhancement, e.g. it is not always known whether the nominal T_c is the temperature at which the crystals actually grow. Similarly, M may well be of direct importance, though the fact that crystals of C_{100} are curved for high T_c, and previous discussions[11] concerning high molecular weight polyethylene, suggest that M cannot be the sole controlling factor.

ACKNOWLEDGEMENT

We thank Professor Sir Charles Frank for his suggestion that the detailed structure of a re-entrant corner site may be important and for his comments on our notation.

Note added in proof

Dr Point has kindly made available to us a manuscript on polyethylene twins by Colet Point and Dosiere. The essential difference between our present approach and theirs is the following. They, as in Part 1 of our work, consider only {110} and (100) faces, for which growth rates are thought to be modified by re-entrant corners, etc. In this paper, Part 2, the same phenomena are discussed in terms of the creation of other faces, e.g. (010), faces oriented at an angle β to (110), and ones perpendicular to the twin plane direction u. This formalism should deal with all the growth rates in terms of one variable, $G(\theta)$, unless, which seems unlikely, Regime I is attained. The difference in approach does not concern whether or not a 'nucleation' model is assumed. Colet *et al.* give an elegant explanation of why the 110 twin plane is not always along the central axis of the crystals. Wittman and Lotz (Figure 6 of ref. 22) show an intermediate twin type (i). The decoration pattern clearly lacks the usual marked orientation in one of the sectors containing the twin boundary. This would be expected if, as we suggest, the face perpendicular to u is molecularly irregular. In this case the fold direction will be less well oriented along the growth face than for {110}.

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