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Electron imaging of twins in polyethylene crystals

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Twins have been identified in the electron image of polyethylene crystals by means of their contrast behaviour on tilting the specimen and using different diffracted beams for dark field microscopy. Both {310} and {110} twinning has been found. The effect of twinning on Moiré fringes has been investigated and experimental observations confirm the twin features to be correctly interpreted.

1. Introduction

The geometry of twinning in orthorhombic polyethylene has been widely discussed and the existence of some of the most favoured modes confirmed by electron diffraction [1-7]. It is perhaps surprising that corresponding observations in the electron image have seldom been reported. Diffraction contrast electron microscopy requires sub-visual illumination conditions to preserve crystal order during prolonged study of a single area, though extensive studies can be made by systematic selection of the dark-field imaging beam [8]. In this procedure the objective aperture is centred around the diffraction spots in succession using minimal illumination for this step as well as for recording such that reflections other than the strong (matrix) spots are rarely recognizable even if visible on the screen, and precision selection is almost impossible. Furthermore, both {100} and {310} twinning gives spots very close to the {110} and {200} matrix spots commonly used for dark-field imaging [2] such that exclusion of unwanted reflections in twin identification studies would require very small objective apertures even if sufficient brightness and time were available for adjustment. The purpose of this paper is to show that the contrast behaviour of twins in dark-field images formed in different beams can be equated to that of striations commonly observed, strongly suggesting twinning as an interpretation for these features.

2. Contrast of twins

2.1. {310} twins

Consider the [001] zone diffraction pattern of an orthorhombic polyethylene crystal with twins on (310) and on (3$\bar{1}$0) planes (Fig. 1). Since the (110) and (3$\bar{1}$0) matrix planes are nearly mutually orthogonal, the ($\bar{1}\bar{1}$0) twin spot corresponding to (3$\bar{1}$0) twinning falls close to the (110) matrix spot, while at the same time both reflections will have very similar misorientations from the Bragg position. Therefore, (3$\bar{1}$0) twinning will produce beams of similar amplitude in an aperture set for dark field from the (110) matrix reflection and there will be poor contrast between neighbouring matrix and twin regions. On the other hand, the third beam falling into this aperture is the (200) reflection corresponding to (310) twinning. The intensity of this beam relative to the others will depend on the orientation of the crystal such that the contrast of (310) twins cannot be predicted in

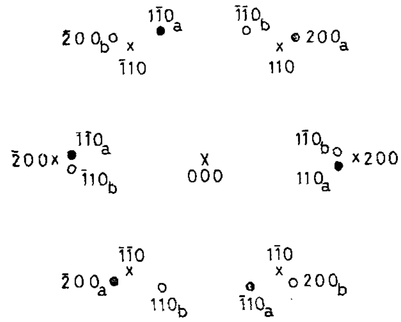

Figure 1 {110} and {200} diffraction spots for (001) oriented polyethylene with {310} twinning. × denotes matrix reflections; ● denotes (310) twin spots: their indices have subscript a; ○ denotes (3$\bar{1}$0) twin spots: their indices have subscript b.

(1 1 0) dark field, and it should be possible to alter their appearance by tilting the specimen. Each of the other {1 1 0} reflections can be similarly analysed. The relative intensities of the three beams falling into an aperture set for (2 0 0) dark field once again depend on the exact orientation of the crystal; both sets of twins could be visible in this case.

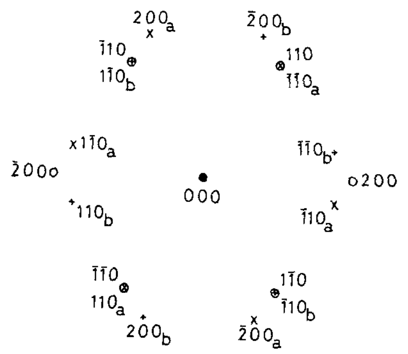

Figure 2 {1 1 0} and {2 0 0} diffraction spots for (0 0 1) oriented polyethylene with {1 1 0} twinning. ○ denotes matrix reflections; × denotes (1 1 0) twin spots: their indices have subscript a; + denotes (1 $\bar{1}$ 0) twin spots: their indices have subscript b.

2.2. {1 1 0} twins

The diffraction pattern corresponding to {1 1 0} twinning is shown in Fig. 2. By the arguments of the previous section, (1 1 0) twins should have poor contrast in (1 1 0) dark field, but have orientation-dependent contrast in (1 $\bar{1}$ 0) dark field. For the objective aperture size usually employed in the present investigation (30 μm), accurate centring for the (2 0 0) matrix beam will ensure collection of a {1 1 0} reflection from each of the {1 1 0} twins such that contrast will again be orientation-dependent. In this case a small displacement of the aperture could result in one or other of the {1 1 0} twin reflections being excluded, hence producing contrast.

The predicted twin contrast behaviour in dark-field electron microscopy is summarized in Table I.

3. Results and discussion

In the course of the current study of the structure of polyethylene crystals grown from dilute solution in xylene many examples of the striations often observed in ⟨1 1 0⟩ and ⟨1 3 0⟩ directions [9] have been found. ⟨1 3 0⟩ striations were found in approximately half of the areas photographed, while the frequency of occurrence of ⟨1 1 0⟩ striations was an order of magnitude smaller. Remembering that the $[hk0]$ direction is coincident with the projection of the $(k\bar{h}0)$ plane onto the (0 0 1) plane, the contrast behaviour of these striations, usually imaged in several beams, has been found consistent with their interpretation as twins in the many images analysed (cf. Table I). Striations were found always to have poor contrast when appropriately directed with respect to the imaging beam, and were insensitive to specimen tilt as required. On the other hand, striations in directions for which twin contrast would be orientation-dependent showed variable visibility, often very strong, and were sometimes altered by changing the specimen tilt (which alters the misorientation from the Bragg condition of different reflections by different amounts). An example of contrast reversal is to be found in Fig. 7. Such observations would not be expected if the striations were associated simply with slip.

3.1. {3 1 0} twins: corrugations

⟨1 3 0⟩ striations are shown in Figs. 3 and 4, and display contrast variations with imaging beam in accordance with Table I. Since only one set of

TABLE I

Twinning plane	Striation direction	Contrast in dark field using reflections shown		
		(1 1 0), ($\bar{1}$ $\bar{1}$ 0)	(1 $\bar{1}$ 0), ($\bar{1}$ 1 0)	(2 0 0), ($\bar{2}$ 0 0)
(3 1 0)	[$\bar{1}$ 3 0]	o.d.	poor	o.d.
(3 $\bar{1}$ 0)	[1 3 0]	poor	o.d.	o.d.
(1 1 0)	[1 $\bar{1}$ 0]	poor	o.d.; a.p.c.	o.d.; a.p.c.
(1 $\bar{1}$ 0)	[1 1 0]	o.d.; a.p.c.	poor	o.d.; a.p.c.

o.d. = orientation dependent.
a.p.c. = aperture position critical.

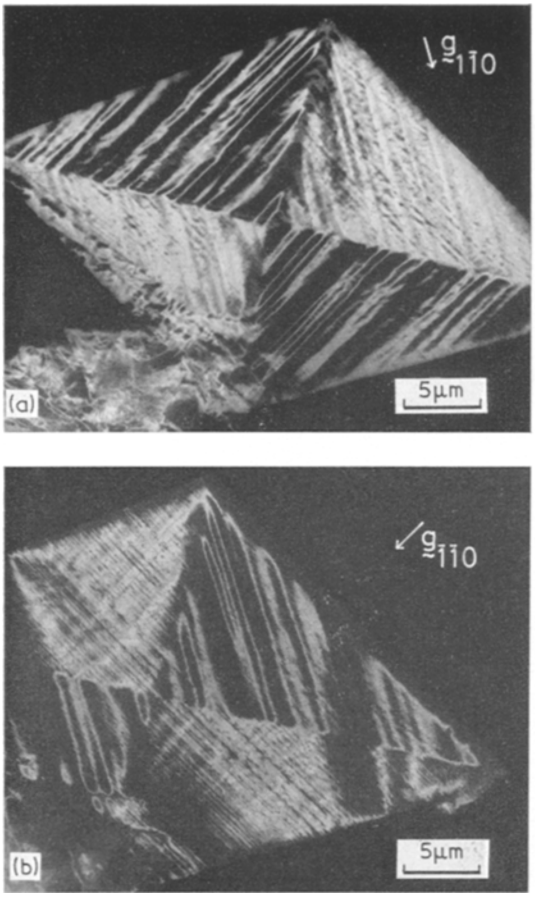

Figure 3 {310} twinning in polyethylene shown in dark-field images using (a) $(1\bar{1}0)$ and (b) $(\bar{1}\bar{1}0)$ beams respectively. Note also the striations in the $[1\bar{1}0]$ direction.

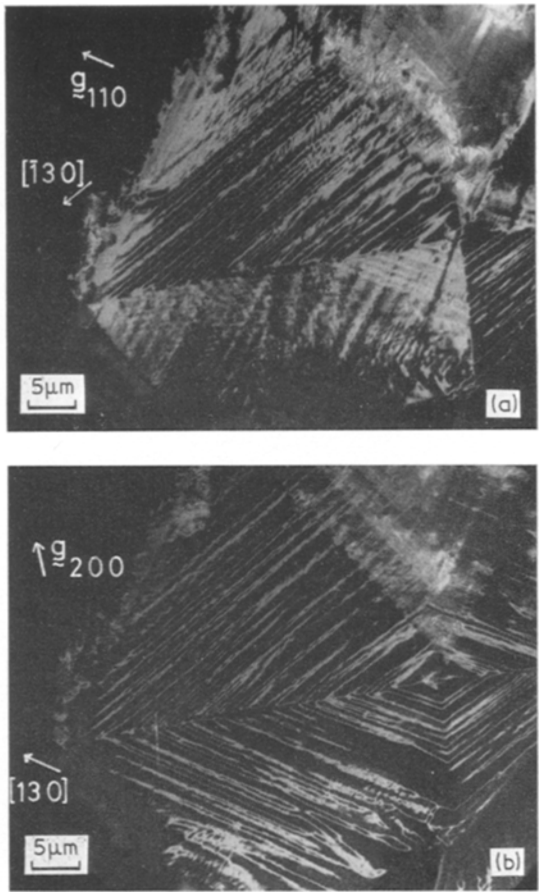

Figure 4 {310} twinning in polyethylene shown in dark-field images using (a) (110) and (b) (200) beams, respectively.

striations occur per sector, (e.g. in the $[\bar{1}30]$ direction in the (110) and $(\bar{1}\bar{1}0)$ sectors, Fig. 5), then the contrast will be expected to vary from sector to sector in addition to the overall brightness, believed to be governed by molecular tilt.

The electron image striations have been found to correspond to corrugations in the crystal which were proved to be present by light optical microscopy [10, 11]. This can be easily reconciled with a twinning interpretation for if the pyramidal fold surface itself obeys the twin transformation the slope will reverse across the {310} boundary. This seems most advantageous with regard to flattening of the crystal, and in no way excludes assistance of chain-tilt or slip mechanisms in the accommodation of the crystal onto the flat support film. It is interesting to note that if the fold plane were of the type

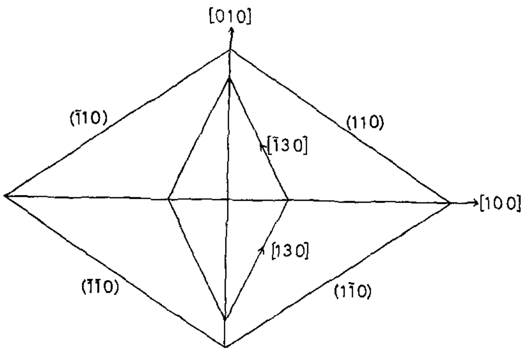

Figure 5 Indexing scheme. Sectors take the indices of the growth faces which bound them.

{314} and if chain tilt of approximately 5° were present, 35% of the crystal in the twin orientation suffices to achieve long range flattening in the absence of slip. These numbers compare favourably with many observations appearing in the literature and show that slip may not always be necessary. It is hence plausible that twinning is a principal mechanism of collapse for the pyramidal crystals when drying out onto a flat surface. On the other hand, the light optical observations of corrugations on crystals free from the stresses accompanying this process suggest this type of twinning may alternatively (or additionally), be a growth phenomenon [10, 11]. ⟨130⟩ striations were never found in the smallest crystals (measuring < 5 μm).

3.2. {110} twins

The contrast behaviour of the striations lying parallel to the [110] direction seen in Fig. 3a and b is consistent with their interpretation as $(1\bar{1}0)$ twins, see Table I. In this case the twinning mode is seen to be independent of sector. Some areas gave diffraction patterns which appeared to be produced by the co-existence of twinning on (110), $(1\bar{1}0)$ and $(3\bar{1}0)$ (Fig. 6).

For further discussion on (110) twinning see [7].

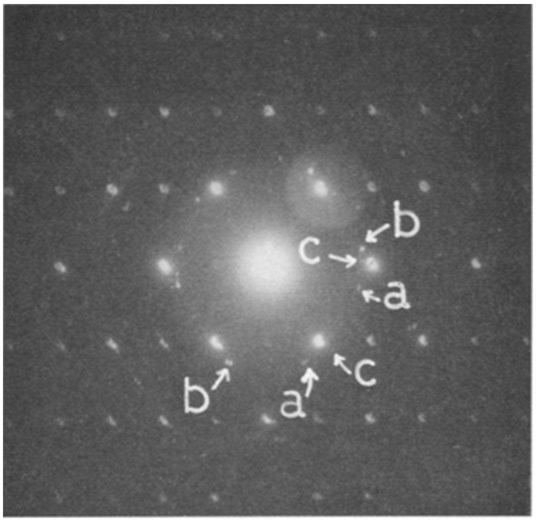

Figure 6 (001) diffraction pattern, showing {110} and {310} twinning. Some of the (110) twin spots have been marked "a", some $(1\bar{1}0)$ twin spots marked "b", and some $(3\bar{1}0)$ twin spots marked "c". Inside the aperture set for (110) dark field can be seen a strong {200} reflection from $(1\bar{1}0)$ twinning plus a weak {110} spot corresponding to $(3\bar{1}0)$ twinning appropriately located to the left of the (110) (cf. Figs. 1 and 2). The diffraction area was approximately 5 × 5 μm² and was selected sub-visually.

4. Effect of twinning on Moiré patterns

4.1. One of the crystals twinned

Detailed discussion of Moiré pattern formation is to be found elsewhere [12]. The presence of twins will have a profound effect on Moiré pattern geometry and contrast, and demands examination. Consider two crystals superimposed to yield a rotation Moiré pattern, and introduce some twins into one of them. In most instances the twinned regions will produce diffraction spots significantly displaced from those of the matrix crystal and hence from an untwinned crystal at a small relative rotation (see Figs. 1 and 2). Even when the twin spot falling nearest to the imaging beam is collected by the aperture the separation from the untwinned crystal beam will be so large that a Moiré pattern produced by interference of these beams would be of such small period as to defeat resolution by the method of recording employed [8]. Moiré contrast would hence effectively disappear in these regions. Such effects are frequently observed and this model may sometimes pertain.

4.2. Both crystals twinned

Polyethylene crystals are easily deformed and can be expected to imitate the irregularities of the substrate to a large degree. This property has been exploited to produce specific localised deformation transferred from a copper substrate [13, 14]. Hence if a polyethylene crystal settles onto a larger one which already contains twins or which subsequently forms them, it would be likely to deform in harmony. In the case of crystals lying in closely similar orientation this deformation will, of course, be most efficiently achieved by means of a similar and coincident twin transformation. If this occurs the two superposed twins will diffract beams of similar mutual angular separation to those produced by the superposed (matrix) crystals. If a pair of such beams falls into the objective aperture set for dark field they may mutually interfere to produce Moiré fringes.

In the case of (110) dark field, (310) twinning would cause (200) twin reflections to fall into the aperture, rotated slightly from the (110) matrix reflections. The Moiré pattern formed by the twin beams would have a smaller period than that produced by the (110) reflections (by the ratio d_{200}/d_{110}). The brightness of such a pattern would depend on the same factors as those discussed above for monolayer crystals, while

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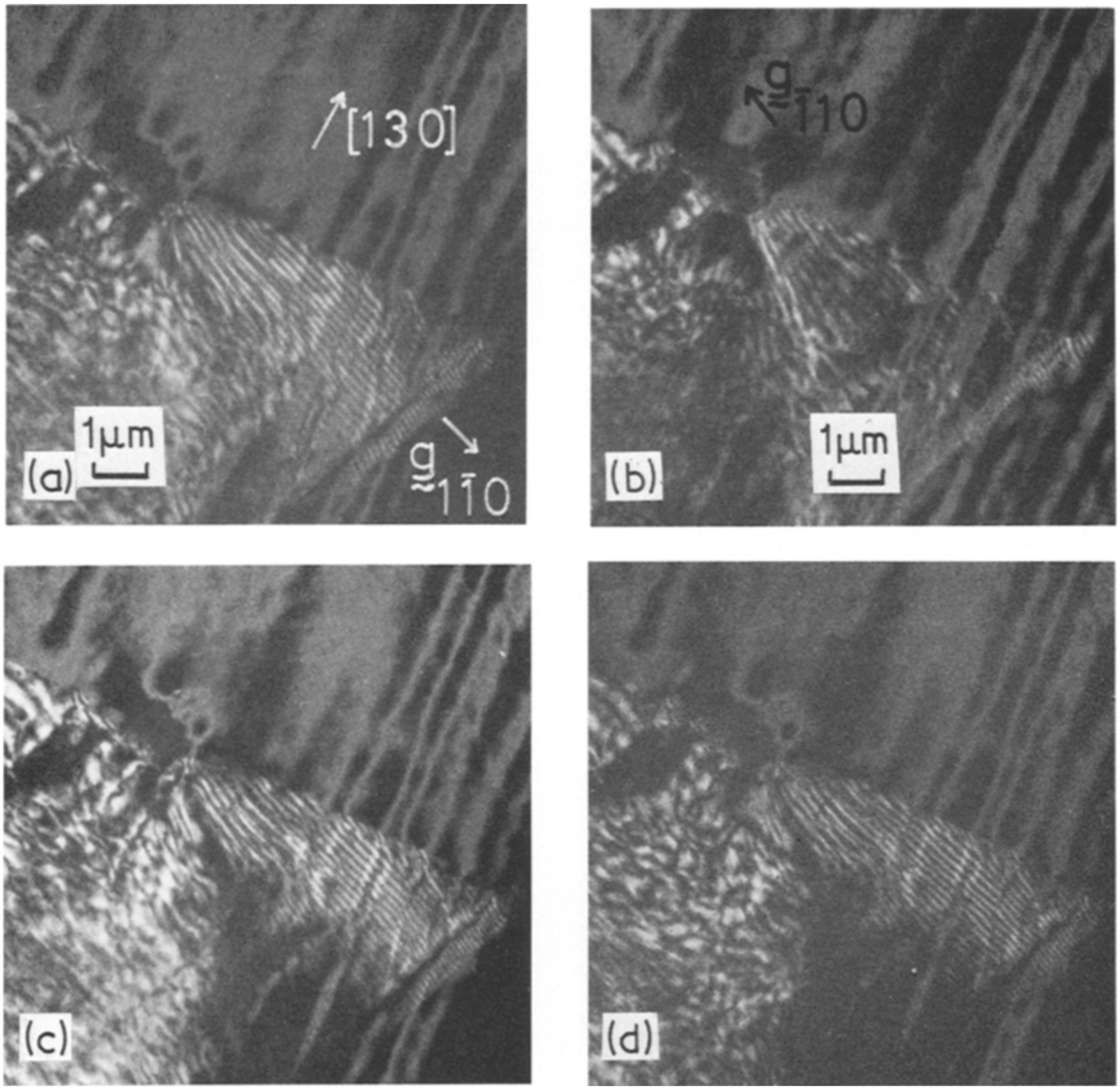

Figure 7 Moiré pattern crossed by $(3\bar{1}0)$ twins. Pairs of images (a)–(b), (c)–(d) and (e)–(f) respectively were taken at slightly different specimen orientations using dark field imaging with the $(1\bar{1}0)$ beam for (a), (c) and (e), or the $(\bar{1}10)$ beam for (b), (d) and (f). Note the approximate reversal of twin contrast comparing (a) and (e).

contrast would depend upon the *relative* amplitudes of the two beams. Good contrast in the regions of overlapping matrix crystals does not necessarily imply the same for the twins since they are imaged in beams diffracted by different sets of planes, which may have a different *relative* orientation. There is much evidence to suggest that the molecular chains tilt by amounts which vary according to crystal size and to the location within the crystal [9, 15, 16], so that it does not follow that pairs of twin reflections of comparable amplitude will be located near to matched pairs of matrix beams. Consequently, on moving into a twinned region the spacing and orientation of the Moiré pattern should change, while brightness and/or contrast may alter.

Other examples may yield different constraints, as for example (310) twinning imaged in $(1\bar{1}0)$ dark field. In this case the twin beams are also from the {110} family and the Moiré period remains the same, though again suffers a small rotation (approximately 15°). Brightness and contrast are determined once more by the detailed orientation of both crystals relative to the incident beam, as discussed above. It should

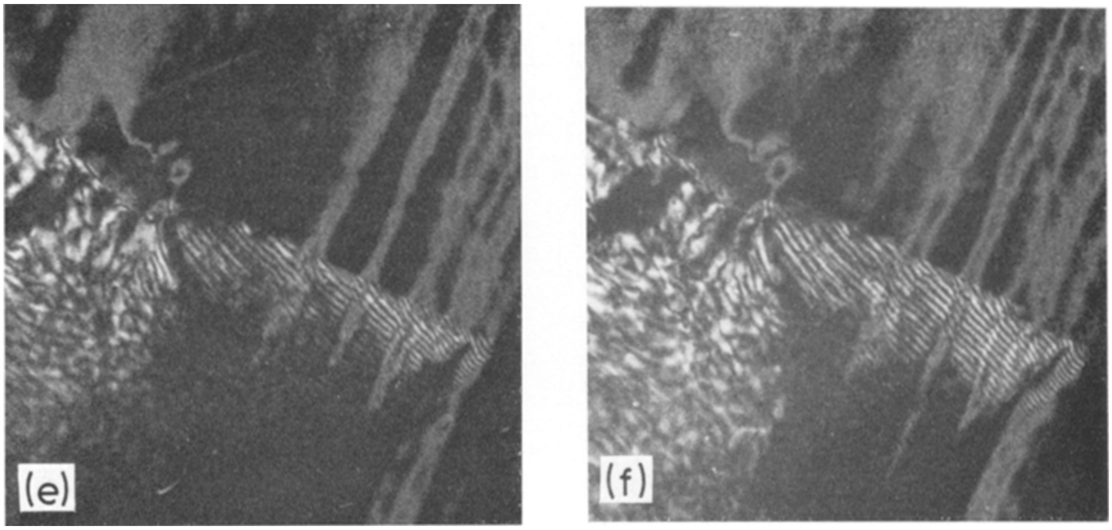

Figure 7 continued.

further be noted that the phase of the Moiré fringes is dependent on the orientation parameter and may change on passing from matrix to twin, despite retention of the same spacing [17, 18]. An example of $(3\bar{1}0)$ twins in a large crystal which cross a bi-layered region containing Moiré fringes is shown in Fig. 7. Images taken in both $(1\bar{1}0)$ and $(\bar{1}10)$ beams and at different specimen orientations are presented. The changes in the Moiré pattern appearance are consistent with the considerations presented above, and provide convincing evidence for the identification of the striations as twins. Note also the reversal of contrast of the striations, expected to be attainable on appropriate tilting (compare Fig. 7a and e).

Similar features to those shown in Fig. 7 have previously been attributed to twinning by Andrews and Voigt-Martin [7], and hence their interpretation stands closer examination.

4.3. Exception

In both cases considered above, namely twinning in one crystal, and twinning in both crystals, Moiré patterns in (110) reflections should be insensitive to (110) twinning with respect to both geometry and contrast since the twin beam is coincident with the matrix beam of equal amplitude.

5. Conclusions

Detailed consideration of the electron image contrast of twins has led to their identification in specimens studied under limiting electron optical conditions. Such features have often been observed previously but sufficient information to achieve recognition of the structural significance was missing. The nature of the corrugations described by others is most eloquently explained, with the fold surfaces undergoing a {310} twin transformation. The behaviour of Moiré patterns crossed by twins provides further supporting evidence for the attachment of a twin interpretation to the striations seen in the image.

Acknowledgement

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