Planar defects in GeSe and GeS crystals

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Planar defects in layered GeSe and GeS crystals grown by vapour transport are studied by transmission electron microscopy. The principal defects are (1 1 0) twins, which appear as narrow parallel bands, and (0 0 1) low-angle grain boundaries, containing networks of boundary dislocations. In order to propose an atomistic model, the structure of the materials is described in terms of hexagonal rings and of trigonal pyramids projected along the c-axis. These units are used for the construction of the model of the twin structure which is free of dangling bonds. The relationship of the defects with the transport properties of the materials is discussed.

1. Introduction

GeSe and GeS are semiconductors with a layered structure of the SnS-type [1]. Within the layers, which normally contain equal numbers of anion and cation atoms, the valence rule is obeyed and, therefore, each layer is electrically neutral. The layers are connected by Van der Waals forces. Single crystals of these materials are grown by vapour transport and are of sufficient size for optical and charge transport studies [2]. If one follows carefully the method of growth given in [2], the quality of the crystals is very good (cleaved (0 0 1) shiny surfaces of $\sim 1 \, cm^2$). However, even in mirror-like surfaces, planar defects are always present in the form of parallel narrow bands. These extended defects, which have been characterized as growth twins, are a feature not only of the bulk but also of thin crystals of these materials [3, 4]. In recent works, Kyriakos and Anagnostopoulos [5, 6] observed two types of anisotropic electrical conductivity, one measured parallel and perpendicular to the walls of the bands within the layer plane and a second in directions parallel and normal to the layers. The first

kind of anisotropy will be directly related to these twins and the second to (0 0 1) twist low-angle boundaries. In addition, layered structures are also promising for their intercalation properties where the twin walls are expected to play an important role. In this work, transmission electron microscopy (TEM) observations of the planar defects in GeSe and GeS crystals are presented and a structural model of their twin boundaries is also proposed.

2. Experimental observations

The crystals of GeSe and GeS were grown by vapour transport; the method of growth and some preliminary TEM observations are presented in references [2] and [4]. The structure is orthorhombic of the space group D_{2h}^{16} (Pmcn) [1]. When the materials are observed with the electron beam normal to the (0 0 1) layers (planar view) the electron diffraction patterns (DP) obtained are of the form shown in Fig. 1. In these DPs the shorter g vectors correspond to the 1 1 0- and 1 $\bar{1}$ 0-type reflections and their sum to the 2 0 0- and 0 2 0-types. The characteristic planar defects which are
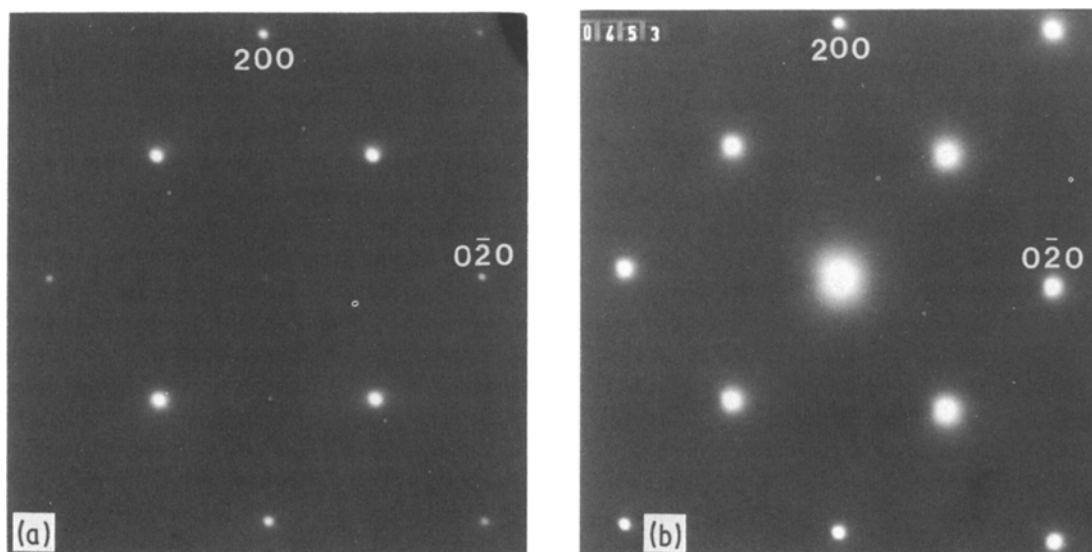

Figure 1 Diffraction patterns of (a) GeSe and (b) GeS single crystals in planar view.
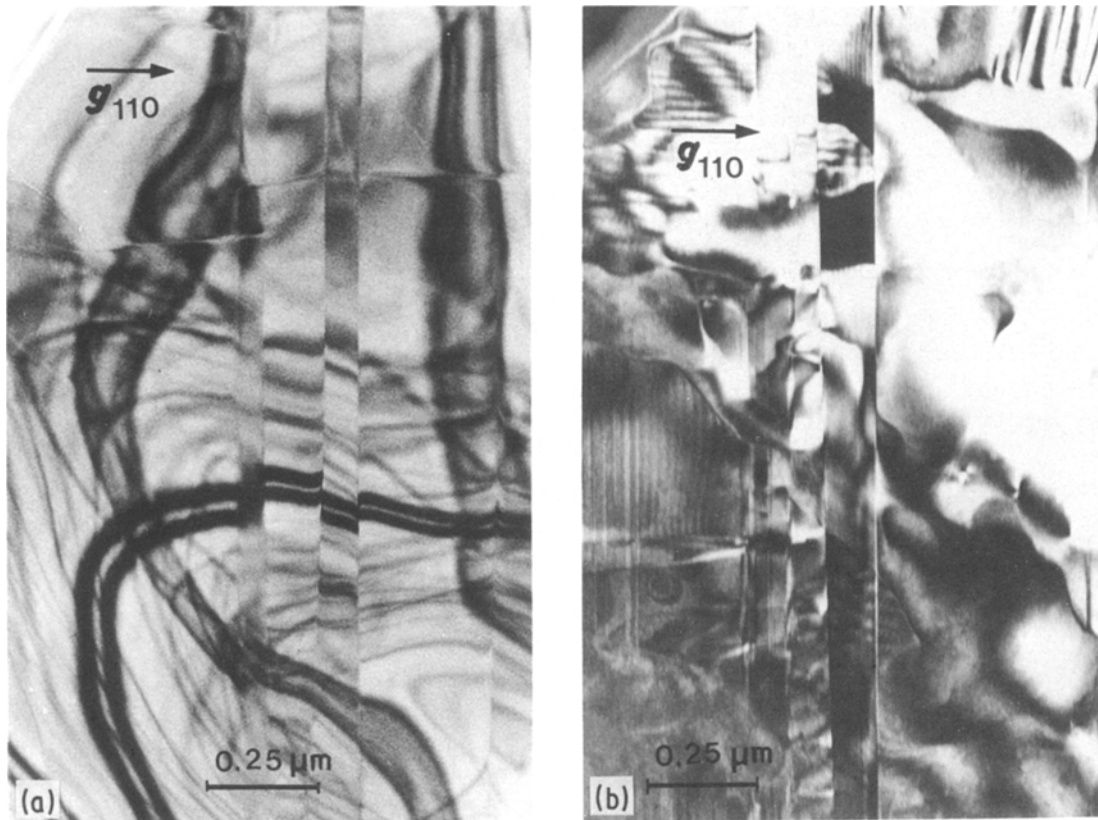
Figure 2 Characteristic twins in (a) GeSe (b) GeS. Note the small deviation of the boundaries from the exact position of the twin planes.

observed in the same orientation are twin boundaries grown in sets of narrow parallel bands (Fig. 2). The boundaries of these defects are almost parallel to the (1 1 0) plane of the crystal, which is also the twin plane. A thorough examination of the boundaries of Fig. 2 reveals that they are not perfect crystallographic planes but they exhibit a small deviation from the exact twin planes and, also, they have segments with slightly bent surfaces. This may be followed by small relative rotations of the adjacent twin crystals about the [0 0 1] axis. The DPs of these twins are shown in Fig. 3. In these micrographs the twin spots are placed in lines parallel to a *g* vector. They are produced by a 180° rotation of the DP about this vector. For this

reason this line should not contain twin spots; the existing ones are due to double diffraction. The two types of twins (1 1 0) and (1 $\bar{1}$ 0) can grow together and this is shown in the pattern of Fig. 4.

GeSe has been also observed with the (0 0 1) layers parallel to the beam (cross-section view). The planar defects which might be expected to be observed in such cross-section images, would be stacking faults, twin boundaries or low-angle grain boundaries (GB). Among these, only the low-angle GBs have been observed. They appear as isolated boundaries but they are, usually, the two successive faces of a small slice of the material embedded within the layered structure or on its surface, as depicted in Fig. 5. Their boundary
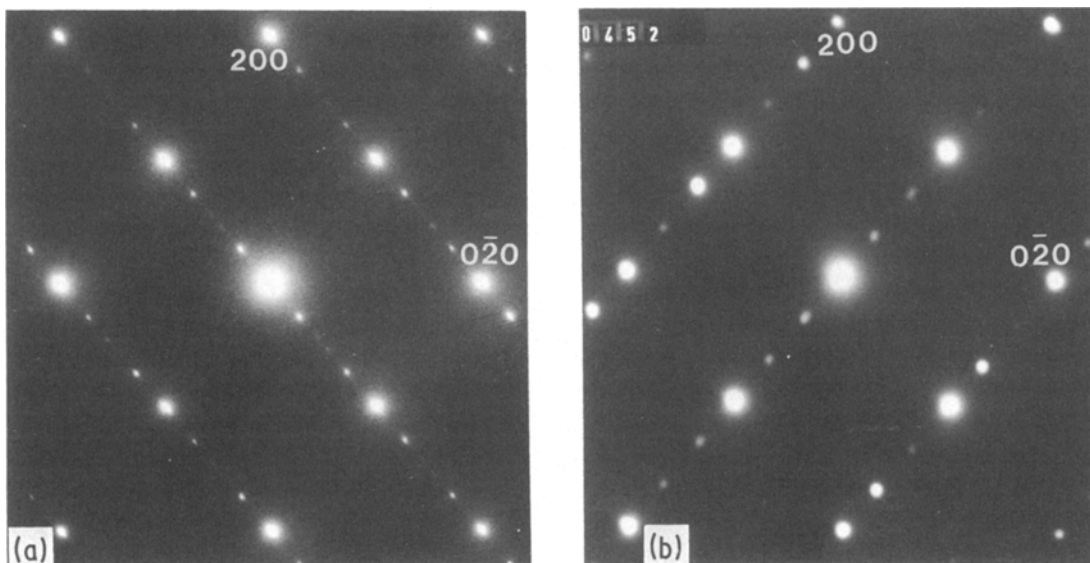

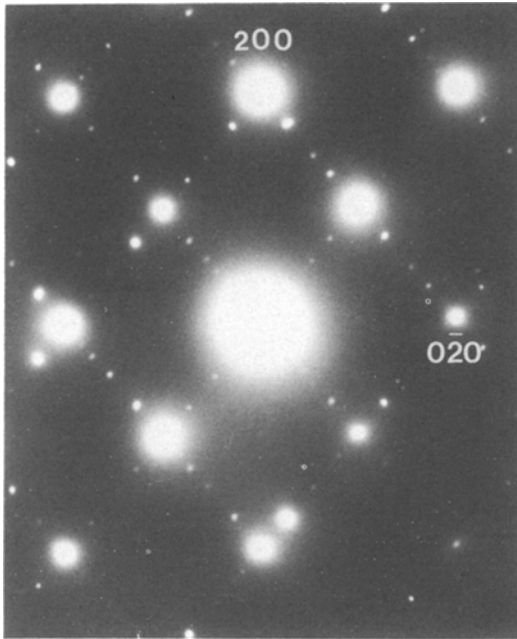*Figure 3* Diffraction patterns of the twin crystals of (a) GeSe and (b) GeS.

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Figure 4 Diffraction pattern from a GeSe crystal forming both (1 1 0) and (1 $\bar{1}$ 0) twins.

planes are always (0 0 1) (the planes of the layers) with a twist character of an angle of about 2°. As indicated in Fig. 5b, the boundary plane can make steps passing from one layer to another. When the rotation angle is small, typical dislocation networks of the twist low-angle GBs are produced, as seen in the micrographs of Fig. 6. As indicated in Fig. 6a, these boundaries can also terminate at dislocations within the material. The

low-angle GBs can be observed also in planar view (Fig. 7). It is more probable that their origin is rather the deformation of the specimen than the growth mechanism. This deformation can be varied along the boundary plane as has been deduced from the deviation of the spacing of the adjacent dislocations.

As mentioned above, small slices of the material can be embedded within the layered structure or alternatively, be formed on its surface. They have, usually, the image of small islands, as shown in Fig. 8a. These islands are grains, which form low-angle twist GBs, but their misorientation angles are higher than 5°. In Fig. 8b, a DP from an area containing islands is presented. The pattern shows misorientations of the order of 10°. The multiple reflections are due to double diffraction in the repeated slices of the material.

3. The structure of the twins

In order to construct a structural model for the twins in GeSe and in GeS, it is necessary to present the structure of these materials in a way that would make such a model more explicit. We choose for the orthorhombic cell the following description

$$a < b < c,$$

that is:

Pmcn with lattice parameters

$a = 0.3827$ nm, $b = 0.4390$ nm, $c = 1.0824$ nm for GeSe [2] and $a = 0.365$ nm, $b = 0.430$ nm, $c = 1.044$ nm for GeS [7]. Four molecules are contained in the unit cell with their atoms at the coordinate
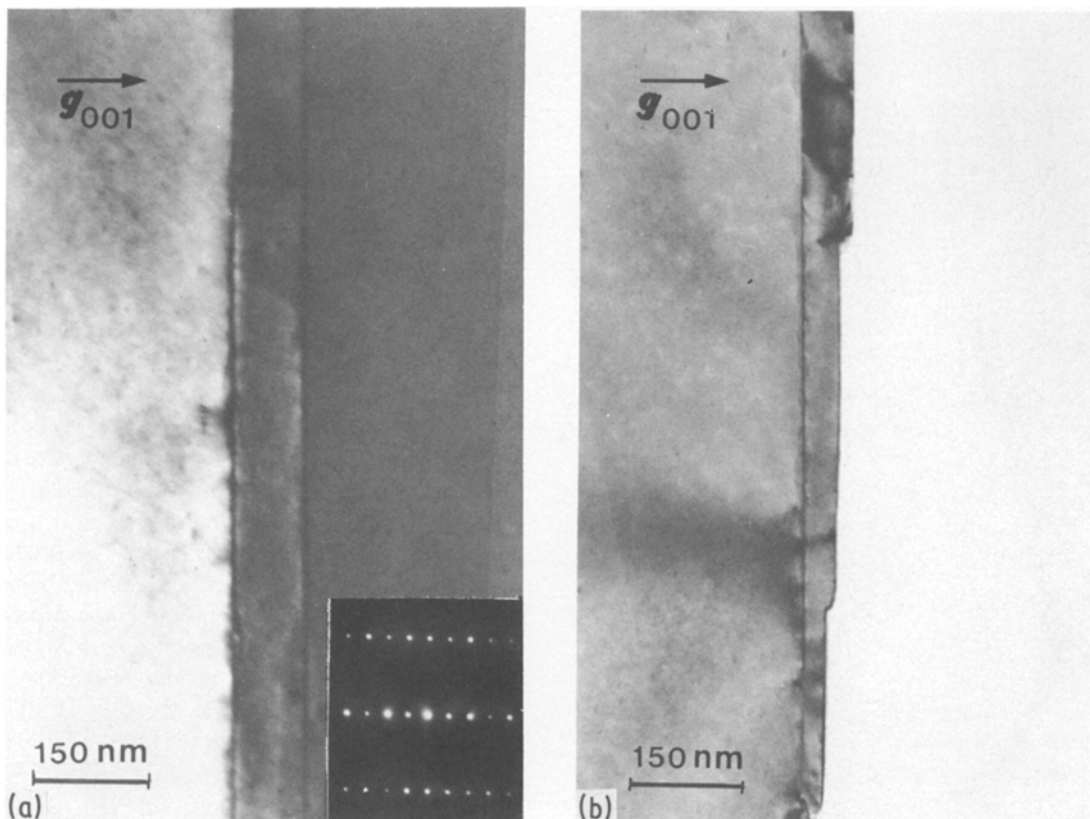

Figure 5 Cross-section images of GeSe low-angle GBs in edge-on position. The inset is the corresponding diffraction pattern. The boundary plane is the (0 0 1) plane. Note that in (b) the right-side is an internal boundary.
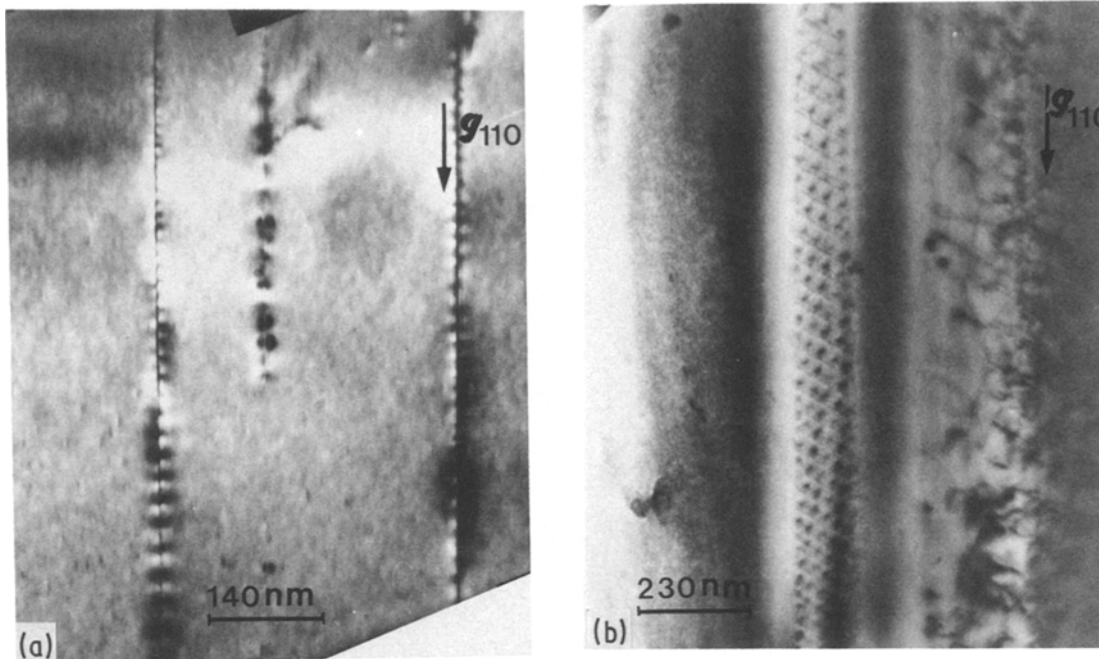
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Figure 6 (a) Low-angle GBs of GeSe in edge-on position. Dislocation arrays are visible. (b) Low-angle GB in an inclined position. Dislocation networks are visible.

positions

$$\pm(\tfrac{1}{4}, y, z), \quad \pm(\tfrac{1}{4}, \tfrac{1}{2} - y, \tfrac{1}{2} + z).$$

For GeSe we have $y(Ge) = 0.111$, $z(Ge) = 0.121$, $y(Se) = 0.500$, $z(Se) = -0.146$ and for GeS $y(Ge) = 0.106$, $z(Ge) = 0.121$, $y(S) = 0.503$, $z(S) = -0.148$. This cell can be considered as a distorted NaCl cell. Four layers of atoms of the undistorted rocksalt structure are contained along the c-axis of the distorted one. However, since the distortion reduces the six

Figure 7 Dislocation network in a twist low-angle GB in planar view in GeSe.

half-bonds acting in the NaCl structure to three single-bonds in GeSe and GeS, each layer of the distorted structure is formed from two successive layers of the undistorted cell. Based on these, the projection of the structure along the c-axis will have the form which is illustrated in Fig. 9. As we can see, the structure is formed by two similar successive layers made by rings of six atoms, 3 Ge and 3 Se (or S). In the ring, the atoms of germanium are situated on two sublevels and the atoms of selenium on two different ones. The two layers can coincide after a 180° rotation of one of them about the [0 0 1] axis and a proper translation. This description is similar to that of a diamond structure along the [1 1 0] axis [8] and simplifies the presentation of GeSe and GeS unit cells composed of eight atoms. The six-ring model is the structural unit which describes the perfect structure of the materials.

Let us now look again at the shape shown in Fig. 9. We can see that the atoms of one kind within the layer can be considered as being situated on the top of trigonal pyramids and each is being bonded with three atoms of the other kind which are located at the corners of the base. We choose selenium atoms for the top and germanium atoms for the base of the pyramid. The projection of the structure along the c-axis, which is presented in Fig. 9, can be made again using these pyramids as basic units. In order to construct the structure of a layer, the pyramids should be placed in two different positions. In the first, the projection of which is illustrated in Fig. 10a, selenium atoms are situated below the plane of the base; they will be indicated with a ($-$) label. In the second, the projection of which is illustrated in Fig. 10b, selenium atoms are situated above the plane of the base; they will be indicated by a ($+$) label. Based on these, the structure of SnS-type structure is also composed of two identical layers of trigonal pyramids which can come in coincidence by the same operation as the one used for
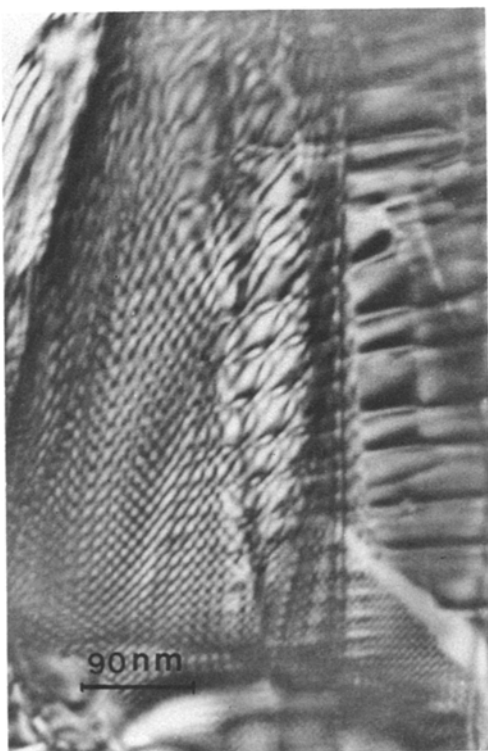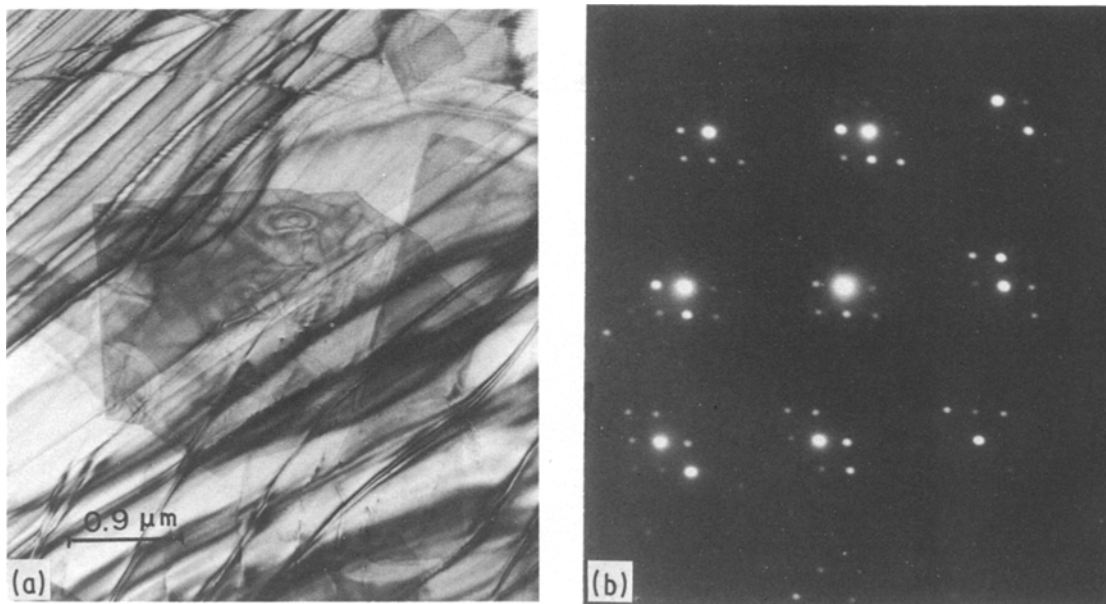
Figure 8 (a) Embedded grains in the form of islands in GeSe. (b) Diffraction pattern from an area containing islands.

the hexagonal rings of Fig. 9. It should be noticed that this pyramid model is for geometrical use and has no special physical significance.

Before we proceed with the construction of the atomistic twin model, we give the twin model in a P-type orthorhombic lattice with parameters a, b and c. Since in orthorhombic structures the twin planes are of the (1 1 0)-type [9] and the lattice is centrosymmetric, the twin relationship is produced by a 180° rotation around an axis normal to the (1 1 0) plane. Such an operation leads to a shape like the one illustrated in Fig. 11. Note that the nodes ABB'A' across the boundary correspond to the nodes of the basal plane of a pseudotetragonal cell.

If we use a matrix $R(\theta)$ to describe the 180° rotation about an axis normal to the $(h\,k\,l)$ plane, we can find three other equivalent descriptions. These are given by

matrices which are the results of the products: $C_{2x}R$, $C_{2y}R$, $C_{2z}R$, where C_{2x}, C_{2y} and C_{2z} are symmetry elements [10]. By expressing the rotation matrix elements as functions of the direction cosines of the rotation axis and of the rotation angle $\theta = 180°$ [11], we find finally that the equivalent descriptions of a twin, in terms of their rotation axes and the corresponding rotation angles, as functions of the h, k, l, in the orthorhombic system are given by

u	v	w	$\cos\theta$
$\dfrac{k}{a^2}$	$\dfrac{k}{b^2}$	$\dfrac{l}{c^2}$	-1
0	l	$\bar{k}$	$\dfrac{2h^2d^2}{a^2} - 1$,
$\bar{l}$	0	h	$\dfrac{2k^2d^2}{b^2} - 1$,
k	$\bar{h}$	0	$\dfrac{2l^2d^2}{c^2} - 1$,

where d is the interplanar spacing

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}.$$

By replacing h, k, l with 1, 1, 0 and giving to the a, b, c the values of the corresponding lattice parameters, the equivalent descriptions of the (1 1 0) twins for the lattices of GeSe and GeS are calculated and the results are listed in Table I.
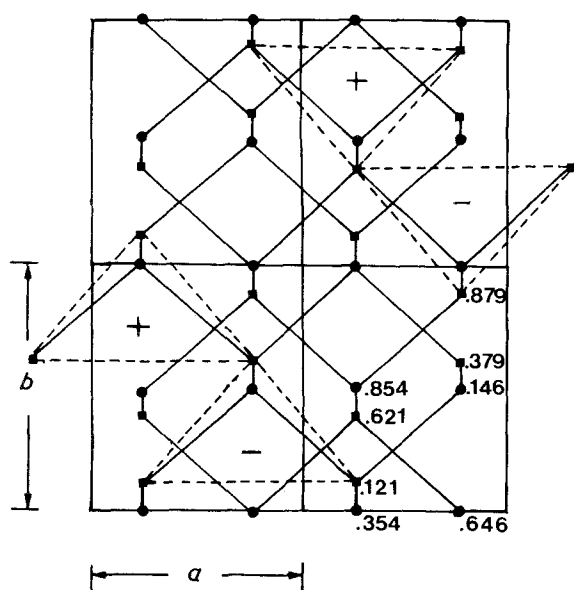

Figure 9 Projection of GeSe structure along the c-axis. The structure is formed by two similar successive layers made by rings of six atoms. In the unit cell the coordinate positions along the c-axis are indicated. (■) Germanium, (●) selenium.

TABLE I Equivalent pairs of rotation axis-angle operations for the description of a twin in GeSe and GeS structures

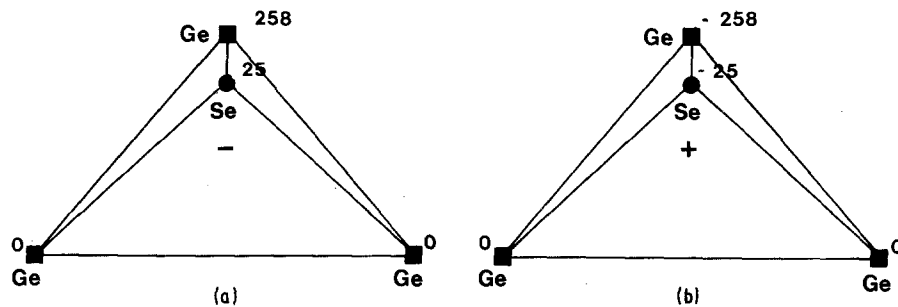| GeSe				GeS			
u	v	w	θ (deg)	u	v	w	θ (deg)
1.31	1	0	180	1.39	1	0	180
0	0	$\bar{1}$	82.16	0	0	$\bar{1}$	80.65
0	0	1	97.84	0	0	1	99.35
1	$\bar{1}$	0	180	1	$\bar{1}$	0	180

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Figure 10 (a) A trigonal pyramid projected along the c-axis with selenium atoms (a) above and (b) below the plane of its base. The relative coordinate positions of the atoms along the c-axis are indicated.

Since the materials consist of strongly bonded double layers with much weaker interlayer bonding we propose, as a twinning process, a mechanism during which the layers do not break for the formation of the twin crystal. This leads to the assumption that a line of atoms (i.e. germanium) is common in both crystals. Thus, among the four equivalent descriptions of the twinning operation, the two about the [0 0 1] axis should be preferred.

In order to give a structural description of the defects, we search for a unit which could lead to (1 1 0) twinning. The construction of this unit is based on the assumption that, within the defects, the material tends to avoid dangling bonds. Thus, the three single bonds which describe the interatomic interactions of every atom should be preserved, as far as possible. A similar process has been followed by Papon and Petit [12] for the construction of the structural units in group IV semiconductors. Variations in the lengths of the bonds and small deformations are allowed and this leads to small changes of the interatomic distances and angles. For the presentation of the atomistic model of the twin we choose the trigonal pyramids. By considering each layer separately, we construct a twin layer by keeping in the original part of the layer a line of germanium atoms, along the [1 1̄ 0] direction, as common boundary to which we connect the twin part after rotating it by 97.84° about the [0 0 1] axis. Such a construction leads to the two twin layers of Fig. 12a,

b which by the proper superposition gives the model of the twin, which is illustrated in Fig. 13 as a model of bonds for the simplification of the drawing.

This twin model seems to be sound since it obeys the symmetry mechanism of twinning. As is illustrated in Figs 11 and 13, due to the geometry of their internal structure, these materials are almost symmetrical over the (1 1 0) plane which can be considered as a plane of pseudosymmetry. Since the structural pattern of Fig. 13 can be formed with only small distortions of the bonds and no broken bonds, this gives an explanation for the occurrence of the (1 1 0) twins. On the other hand due to the much weaker interplanar bonding the dislocations lie parallel to the layers and the low-angle boundaries are formed by the planar arrangements of these dislocations in the form of networks.

4. Conclusion

As we see from the model, the boundary which is extended parallel to the twin plane has a structural width of a few interplanar spacings, defined by an area composed by an array of deformed structural units. The two twin parts also exhibit a rigid-body translation.

This model, which has no dangling bonds, is in agreement with many of the observations of [6] according to which the (1 1 0) type twin walls are almost electrically passive. Their small barrier height is due to the deformation in the area of their boundaries. Their effective thickness of several nm is also anticipated. These twins are responsible for the electric
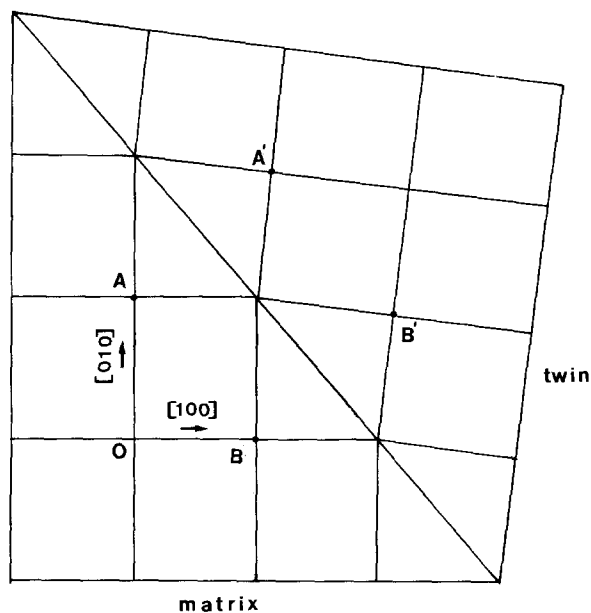

Figure 11 The lattices of a (1 1 0) twin in a P orthorhombic lattice. The nodes ABB′A′, across the boundary, define the basal plane of a pseudotetragonal cell.
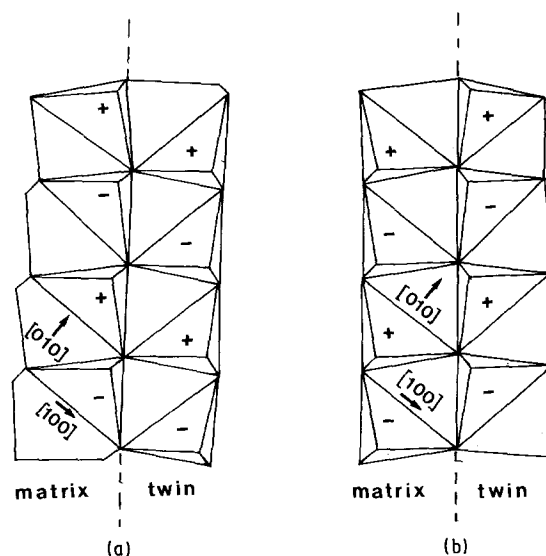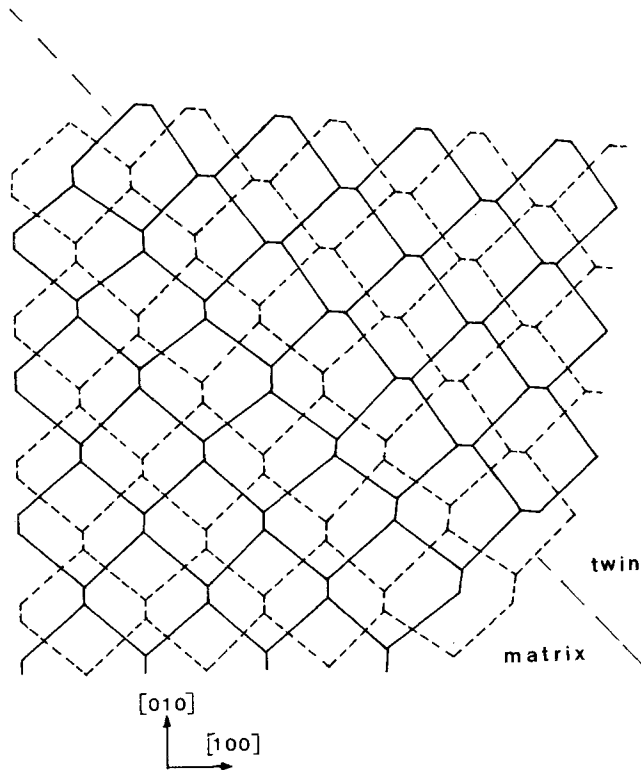

Figure 12 (a) The first and (b) the second layer of the matrix–twin structure.

Figure 13 A possible twin model for GeSe and GeS based on the proper superposition of the twin layers of Fig. 12.

[010]

[100]

anisotropy within the (0 0 1) layer. On the other hand, another kind of electric anisotropy parallel and perpendicular to the layer planes of GeSe crystals has been observed in [5]. The resistivity at low temperatures is significantly greater parallel to the c-axis than perpendicular to it. This can be mainly attributed to the canonical sequence of the low-angle grain boundaries which are parallel to the layer planes and contain dense arrays of boundary dislocations. From these we notice that it would be very interesting to investigate also the electrical properties of GeS, in relation to their structural ones, since GeS and GeSe exhibit very similar characteristics when observed by TEM.

Acknowledgement

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