

towards the base of an etch pit ([1], Fig. 3). They state that they derive this from a back-reflection Laue photograph using the fact that the  $(+y+z)$  quadrant in the mirror plane contains "a pseudo three-fold axis and the  $(-y+z)$  quadrant a pseudo four-fold axis". Lacking any further definition of these axes, it seems sufficient to point out that this result differs from that obtained by the indexing of a Laue photograph in Table II and also their results differ from those of all other workers whose papers we are aware of.\*

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\*Dr. Saunders kindly sent us a complete description of his technique of orientation. He also drew our attention to the paper by R. D. Brown, R. L. Hartman and S. H. Koenig (*Phys. Rev.* **172** (1961) 598) in which a similar method was employed. Back-reflection Laue patterns are obtained by directing the X-ray beam along a mirror plane and at right angles to  $[111]_{rh}$ . The distinction between  $\{011\}_{rh}$  (pseudo four-fold) lying  $32^\circ$  (for As) from the X-ray beam and  $\{100\}_{rh}$  (pseudo three-fold) lying  $18^\circ$  (for As) from the X-ray beam, is easily made by inspection or measurement. The direction  $+Y$  is thereby established. We have redetermined our orientation using this technique and find that our results are unchanged. We understand that Dr. Saunders has resolved the matter and is publishing his results.

## Conversely oriented etch pits in A7 structure semimetals

Extensive studies have been made of etch pits produced on the (111) cleavage plane of the A7 structure semimetals [1-9]. Apparent discrepancies in the orientation of these pits have been mentioned [6, 8] and the present concern is to examine this question further. Using many of the etching reagents quoted in the literature, we have examined the orientation of etch pits on single crystals, grown in this laboratory, of bismuth, arsenic, antimony, an arsenic (25.5 at.%) - antimony alloy and an antimony-(2 at.%) germanium alloy.

Crystals were aligned using the symmetry shown on Laue back-reflection photographs. The conventional definition of the cartesian axial set with respect to the Bravais lattice, used in this work and in many previous studies of bismuth [10, 11], arsenic [12, 13], antimony [10, 14] and the arsenic-antimony alloy [8] is illustrated in, among others, Figs. 1 of references [6-8];

Calvert and Taylor [15] also use this convention in the preceding communication. To orient the crystals, the  $+y$  and  $-y$  directions need to be determined subsequent to and consistent with an arbitrary choice of a  $+z$  direction along the trigonal axis. This can be achieved by reference to the fact that the A7 structure is closely related to a simple cubic structure from which it can be obtained by applying two independent, small distortions [12, 14]; the normals to the  $\{100\}_{fer}$  planes (in Miller indices referred to the face centred rhombohedral cell) exhibit pseudo-fourfold symmetry and the normals to the  $\{\bar{1}11\}_{fer}$  planes pseudo-threefold symmetry [11, 14, 7]. Referred to the primitive rhombohedral unit cell, these pseudo-axes are the normals to the  $\{011\}_{prh}$  and  $\{100\}_{prh}$  planes respectively. Hence the quadrant in the mirror plane formed by the  $+y$  and  $-z$  axes (and the  $-y$  and  $+z$  axes) contains a pseudo-fourfold axis and that formed by the  $+y$  and  $+z$  axes (and the  $-y$  and  $-z$  axes) contains a pseudo-threefold. When a back reflection photograph is taken with the X-ray beam

incident along a bisectrix axis onto a crystal with its cleavage plane horizontal, a pattern with mirror symmetry is obtained; the photograph also shows a spot corresponding to the pseudo-threefold reflection. An example for bismuth is to be found in Fig. 3 of reference [6]. If the  $+z$  direction is chosen to be the outward normal to a cleavage surface, then the  $+y$  direction is determined since the pseudo-threefold reflection

must be in the  $+y+z$  (or the  $-y-z$ ) quadrant. The angles between the pseudo-axes and the  $+y$  axis are listed in Table I.

Oriented crystals were then etched using the reagents listed in Table II, and the pits – on that cleavage face with the previously defined  $+z$  axis emerging from it – were examined. For a particular etchant on a given material, the pits consistently had a definite orientation. In all cases the sides of the etch pits were parallel to the binary directions and pits on the  $-z$  cleavage face ( $-z$  axis emerging from the face) were inverted with respect to those on the  $+z$  face, as required by the inversion axis of the  $\bar{3}m$  point group. However, Table II shows that with different etchants on a given material, two distinct and opposite orientations of triangular pits can be found; in some cases the pits were such that the  $+y$  axis pointed outwards from the pit centre normal to a base of the triangle (type A), and in others the  $+y$  axis pointed outwards through an apex of the triangle (type B). It should be noticed that even when a particular etch is used on different materials, the pits

TABLE I Angles between pseudo-axes and  $+y$  axis in the A7 structure semimetals.

Material	Pseudo-threefold:	Pseudo-fourfold:
	angle between $[2\bar{1}1]_{prh}$ and the normal to $(100)_{prh}$	angle between $[2\bar{1}1]_{prh}$ and the normal to $(100)_{prh}$
As	17.167°	31.717°
Sb	18.317°	33.496°
Bi	18.366°	33.578°
As(25.5 at. %)–Sb	17.984°	32.933°

TABLE II Details of etching and orientation of the pits obtained.

Material	Etching Reagent	Ref*	Orientation of pits
	Composition		
Arsenic	10% Iodine in methanol	[4]	Type B
	CH <sub>3</sub> COOH, HF, HNO <sub>3</sub> , HCl, Br <sub>2</sub> (24:1:2:1:1)	[4]	Type B
	CH <sub>3</sub> COOH, HF, HNO <sub>3</sub> (1:2:1)	[5]	Type A
Antimony	CH <sub>3</sub> COOH, HF, HNO <sub>3</sub> , Br <sub>2</sub> (3:3:5:1)	[1]	Type A
	CH <sub>3</sub> COOH, HF, HNO <sub>3</sub> , HCl, Br <sub>2</sub> (24:1:2:1:1)		Type A
	CH <sub>3</sub> COOH, HF, HNO <sub>3</sub> , Br <sub>2</sub> (28:4:5:3)	[3]	Type A
Bismuth	1% iodine in methanol	[2]	Type B
	33% HNO <sub>3</sub> in water	[6]	Type A
Arsenic (25.5 at. %)–antimony alloy	CH <sub>3</sub> COOH, HF, HNO <sub>3</sub> (3:3:5) and a few drops of bromine	[8]	Type A
	CH <sub>3</sub> COOH, HF, HNO <sub>3</sub> , HCl, Br <sub>2</sub> (24:1:2:1:1)		Type A
Antimony-(2 at. %)–germanium alloy	CH <sub>3</sub> COOH, HF, HNO <sub>3</sub> , Br <sub>2</sub> (3:3:5:1)		Type A

\*The references indicate the published work where the etching reagent has previously been used.

produced on each do not necessarily have the same orientation; for instance the bromine etch of reference [4] produces pits on arsenic with the opposite orientation to those it produces on antimony and the arsenic-antimony alloy.

These findings account for the apparent discrepancies in the orientation of etch pits found by different workers and previously suggested to be due to incorrect definition or identification of axes [6, 8]. In particular it explains the difference in the orientation of the pits obtained by Shetty and Taylor [4] and Calvert and Taylor [15], from those found in these laboratories on arsenic [7], antimony [7] and the arsenic-antimony alloy [8]. Also accounted for are the differences in orientation between the pit orientations on bismuth [2, 6]. Since the etch pit orientation depends on the reagents used, extreme care must be taken if etch pits are to be employed for assignment of the sense of the  $y$ -direction in a crystal. Hexagonal type pits have been reported on arsenic [5] and on bismuth [9]; plausibly, these might represent an intermediate form between the two triangular extremes. The further question of whether all the reagents used give etch pits that mark the points of emergence of all dislocation types on the cleaved surfaces has not yet been resolved.

Variations in the orientation of etch pits have been reported for certain other materials, including LiF [16], NaCl [17], Calcite [18], diamond [19, 20], apophyllite [21], GaSe [22], and silver [23]. It has been suggested [16, 20, 24] that such changes in orientation arise from the introduction of a "poison" into the etchant causing the dissolution rate in particular crystallographic directions to be inhibited. In the present case, it is the difference of anisotropies of dissolution rate of the different etching reagents which produce the various types of pit.

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