8. F. HARGREAVES and R. J. HILLS, *J. Inst. Metals.* **41** (1929) 257.

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Assignment of axes to arsenic and other rhombohedral crystals of the A7 structure type

Over the last decade, there has been much interest in the physical properties of the group V elements (arsenic, antimony and bismuth) and the literature abounds with publications on the subject. Recently, Akgöz and Saunders [1] have raised the question of the necessity for assigning a unique orthogonal axial set when describing such physical properties. Previous workers, Hatori [2], Kosevich [3], and Shetty and Taylor [4] were criticized for using an erroneous definition of a right-handed, orthogonal axial set which, it was claimed, results in incorrect assignment of the basic crystallographic directions. It is incumbent upon us to rebut or accept this criticism. The defence of our position is based on a fresh determination of the orientation of etch pits on cleaved complementary surfaces of an arsenic crystal. In order to clarify the point for future workers in the field, we present for the first time a concise and complete description of the crystallography with reference to three axial systems commonly used by previous workers. Our experimental work refers specifically to arsenic but the treatment and conclusions have direct applicability to other materials with the rhombohedral point group $\bar{3}m$.

The crystallographic data for arsenic are given in Table I. The original description of the structure by Bradley [5] was referred to a face-centred rhombohedral cell (fcr). The angles calculated by Bacon, Heckscher, and Crocker [6] also refer to this cell. The most recent and accurate determination of the crystal structure by Schiferl and Barrett [7] is referred to a primitive rhombohedral cell (rh) and a hexagonal cell (hex). The point group symmetry $\bar{3}\ 2/m$ and space group symmetry $R\bar{3}m$ remain unchanged in each description. An infrequently used body-centred rhombohedral cell [8] related to the primitive rhombohedral cell by the transformation $0\,1\,1/1\,0\,1/1\,1\,0$ is omitted from Table I.

Fig. 1 is a projection of the arsenic structure on the $(1\,1\,1)_{rh}$ plane. The three cells are shown together with pertinent crystallographic data. The origin lies in the paper and the positive directions of the three primitive rhombohedral axes, a_1, a_2 and a_3 are upwards. It must be stressed that there are three possible ways of assigning a_1, a_2 and a_3 in that any one of these directions can be designated a_1 but having done that, the choice for a_2 and a_3 is fixed. (The operation of the centre of symmetry results in another option which is considered later.) This set of rhombohedral axes or any one of the related axial sets is sufficient to set up a Cartesian axial system to describe any tensor property of materials crystallizing with the A7 structure

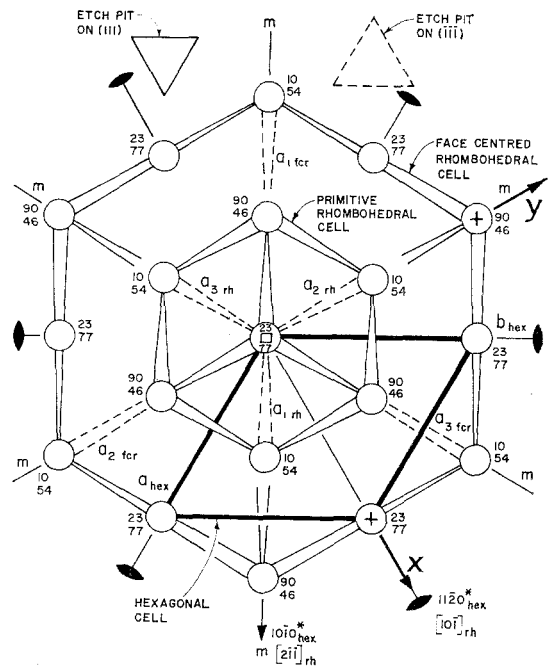

Figure 1 The rhombohedral arsenic structure projected onto $(1\,1\,1)_{rh}$. The atoms (open circles) are labelled with the values of their parameters (numerically $x = z$ for rhombohedral or hexagonal cells) referred to the origin (small square) in the centre; crosses (+) mark the lengths assigned to x and y in the Cartesian axial system.

TABLE I Crystallographic data for arsenic.

Space group ([10] p. 273)	$R\bar{3}m$ (D_{3d}^5) No. 166		
Symmetry elements ([10] p. 27)	An inversion triad axis normal to $(111)_{rh} \equiv (0001)_{hex}$	+ Three two-fold axes along $\langle 10\bar{1}\rangle_{rh} \equiv \langle 11\bar{2}0\rangle_{hex}$	+ Three mirror planes normal to $\langle 10\bar{1}\rangle_{rh} \equiv \langle 11\bar{2}0\rangle_{hex}$
	Rhombohedral cell	Hexagonal cell (obverse setting) ([10] p. 20)	Face-centred rhombohedral cell
Cell parameters	$a = 4.132$ Å $\alpha = 54.126°$	$a = 3.7589$ Å $c = 10.5475°$	$a = 5.5865$ Å $\alpha = 84.633°$
Atoms/cell	2	6	8
Cell volume, Å^3	43.04	129.1	172.3
Atom parameters	$2(c) \pm xxx$ $x = 0.22707$	$6(c)$ $00z + (\frac{1}{3}\frac{2}{3}\frac{2}{3}, \frac{2}{3}\frac{1}{3}\frac{1}{3})$ $z = 0.22707$	$8(c) \pm xxx$ $+(0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0)$ $x = 0.22707$
Transformation matrix in terms of primitive rhomb.	1 0 0 0 1 0 0 0 1	1 −1 0 0 1 −1 1 1 1	−1 1 1 1 −1 1 1 1 −1
Inverse transformation matrix	1 0 0 0 1 0 0 0 1	$\frac{2}{3}$ $\frac{1}{3}$ $\frac{1}{3}$ $-\frac{1}{3}$ $\frac{1}{3}$ $\frac{1}{3}$ $-\frac{1}{3}$ $-\frac{2}{3}$ $\frac{1}{3}$	0 $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ 0 $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ 0
Transformation* matrix to cartesian axial system	1 0 −1 $-\frac{2}{3}$ 0 $-\frac{2}{3}$ 1 1 1	1 1 0 $-\frac{2}{3}$ $\frac{2}{3}$ 0 1 1 1	$-\frac{1}{2}$ 0 $\frac{1}{2}$ $\frac{1}{3}$ $-\frac{2}{3}$ $\frac{1}{3}$ 1 1 1

*Axial lengths x and y chosen to end at points in $(111)_{rh}$ marked by a cross (+).

type, provided that the appropriate transformation matrix is used. Fig. 1 includes a Cartesian axial system identical with that explicitly illustrated by Hatori [2] which in turn accords with prior convention [8]. In this, $+y$ is the projection of a_{2rh} on the $(111)_{rh}$ plane; $+x$ lies in the (111) plane and between the projections of $+a_1$ and $+a_2$ on the same plane; $+z$ is directed along [111] and completes a right-handed system. There are three such systems depending on the original choice of a_1 plus three more related by the centre of symmetry. The location of a_1, a_2 and a_3 on a specific cleavage face of arsenic for example is straightforward. A back-reflection Laue photograph taken with the beam normal to the (111) cleavage face will show 3-fold symmetry plus three mirror planes {plane group 3m ([10], page 40)}. Any great circle through the centre containing one of the mirror planes will serve to identify the positive direction of the axes, a_i, of the rhombohedral cell. It will be seen from Fig. 1 that the positive direction of the rhombohedral a_1 axis when projected onto $(111)_{rh}$ coincides with the a^* $(10\bar{1}0^*$ direction) in the lattice reciprocal to the hexagonal cell ([10], page 14). A scrutiny of the hexagonal indices in Table II shows that the reflections with h positive must have $l = 3n + 1$ to satisfy the condition $-h + k + l = 3n$ for the obverse setting of the hexagonal cell. This quadrant unambiguously fixes the $+a_{rh}$ direction.

The observed Laue reflections are recorded in Table II along with the calculated angles. The cross-angles given in Table III confirm the indexing. The etch-pit orientation on $(111)_{rh}$ is drawn in Fig. 1. This agrees with our previous observations [4] and with the orientation explicitly given by Hatori [2] and Tester [11]. The three strongest Laue spots are $\{445\}_{rh}$ and they

TABLE II Indexing of one asymmetric portion of a back reflection Laue photograph normal to the $(1\,1\,1)_{rh}$ face of arsenic. ϕ is azimuthal angle, positive anticlockwise; ρ is angle between $(1\,1\,1)_{rh}$ and $(hkl)_{rh}$. Photo viewed looking down X-ray beam towards (1 1 1) cleavage face.

ϕ_{obs}	ρ_{obs}	I_{obs}	ρ_{calc}	$(hkl)_{rh}$	$(hkl)_{hex}$	$(hkl)_{rcr}$
0	10½	w	10.788	566	$\bar{1}01.17$	755
0	13	m	13.028	455	$\bar{1}01.14$	644
0	16	s	16.409	344	$\bar{1}01.11$	533
0	22	vw	22.044	233	$\bar{1}018$	422
0	27	m	26.490	355	$\bar{2}02.13$	733
			*(90.0	$\bar{2}11$	$\bar{1}010$	$2\bar{1}\bar{1}$)
30	17	vw	17.313	567	$\bar{1}\bar{1}2.18$	864
30	20	w	20.508	456	$\bar{1}\bar{1}2.15$	753
30	25	vvw	25.059	345	$\bar{1}\bar{1}2.12$	642
			*(90.0	$\bar{1}01$	$\bar{1}\bar{1}20$	$10\bar{1}$)
60	11½	ms	11.445	556	$0\bar{1}1.16$	664
60	14	vs	13.992	445	$0\bar{1}1.13$	553
60	18	vw	17.949	334	$0\bar{1}1.10$	442
60	21	vw	20.862	557	$0\bar{2}2.17$	773
60	25	w	24.833	223	$0\bar{1}17$	331
60	30½	m	30.497	335	$0\bar{2}2.11$	551
			*(90.0	$\bar{1}\bar{1}2$	$0\bar{1}10$	$11\bar{2}$)
90	17	w	17.312	657	$1\bar{2}1.18$	684
90	20	m	20.508	546	$1\bar{2}1.15$	573
			*(90.0	$0\bar{1}1$	$1\bar{2}10$	$01\bar{1}$)
180	11½	ms	11.445	655	$10\bar{1}.16$	466
180	14	vs	13.992	544	$10\bar{1}.13$	355
180	18	vw	17.949	433	$10\bar{1}.10$	244
180	21	vw	20.862	755	$20\bar{2}.17$	377
180	25	w	24.833	322	$10\bar{1}7$	133
180	30½	m	30.497	533	$20\bar{2}.11$	155
			*(90.0	$2\bar{1}\bar{1}$	$10\bar{1}0$	$\bar{2}11$)

*Direction on equator of stereographic projection. Not observed on Laue photograph.

lie at the apices of an equilateral triangle which coincides with the traces on $(1\,1\,1)_{rh}$ of the trigonal pyramidal etch pits.

A complementary cleavage face $(\bar{1}\,\bar{1}\,\bar{1})_{rh}$ from the same crystal, whose orientation relative to the (1 1 1) face can be established by reference to a dislocation network or equally definitely, to any physical mark on it, gives a Laue photograph and etch pit orientation related to those of the first face examined, by a centre of symmetry. In Fig. 1, the solid and dotted triangles illustrate the relative orientations of pits on complementary (1 1 1) and $(\bar{1}\,\bar{1}\,\bar{1})$ surfaces respectively. (The argument is equally applicable to the front and rear {1 1 1} surfaces of a single crystal.) Due to the centre of symmetry, no distinction between a (1 1 1) and $(\bar{1}\,\bar{1}\,\bar{1})$ face is possible when a single cleavage face is examined and a definition of axes is always possible which permits the face to be indexed $(1\,1\,1)_{rh}$ with Laue indexing as in Table II. The observed etch pit orientation is then as indicated by the solid triangle in Fig. 1.

TABLE III Calculated and observed values for selected interplanar angles (Laue photograph as in Table II)

$(h_1k_1l_1)_{rh}$	$(h_2k_2l_2)_{rh}$	ρ_{obs}	ρ_{calc}
344	556	14	14.483
344	445	15½	15.212
344	546	26	26.042
445	556	2½	2.547
445	546	10¾	10.829
445	655	21½	22.021
445	544	24	24.173

An interesting situation arises when a pair of complementary cleavage faces are etched and photomicrographs viewed side by side (e.g. [4], Fig. 1, [1], Fig. 6). The apparent relative orientation of the etch pit traces in the two halves of the composite photograph will depend upon the orientation of their junction line relative to the symmetry elements of the arsenic structure. Thus, if the junction line is a mirror plane of the arsenic structure the etch pit traces on (1 1 1) appear to be rotated 60° relative to one another ([4], Fig. 1). If the junction line is a two-fold axis of the arsenic structure the etch pit traces appear to be identically orientated ([1], Fig. 6). A junction line in a general direction of the arsenic structure gives an apparent relative pit orientation on the two photographs intermediate between the extremes. This situation can give rise to misunderstanding and Akgöz and Saunders ([1], p. 399) seem to allude to it when they mention confusion in the literature over the observation of inversion symmetry in pits obtained on complementary faces.

It is apparent that many independent workers have used crystallographically conventional axes and Laue patterns to derive results which are consistent with our own and adequate for their respective purposes but, like outselves up to this point, have never explicitly detailed the derivation of the axial set. Akgöz and Saunders whilst correct in their arguments, reach a conclusion which places the $+y$ axis pointing

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.*

References

1. Y. C. AKGÖZ and G. A. SAUNDERS, *J. Mater. Sci.* **6** (1971) 395.
2. T. HATORI, *J. Phys. Soc. Japan* **24** (1968) 762.
3. V. M. KOSEVICH, *Societ Phys. Crystallog.* **5** (1961) 715.
4. M. N. SHETTY and J. B. TAYLOR, *J. Appl. Phys.* **39** (1968) 3717.
5. A. J. BRADLEY, *Phil. Mag.* **47** (1924) 657.
6. D. J. BACON, F. HECKSCHER, and A. G. CROCKER, *Acta Cryst.* **17** (1964) 760.
7. D. SCHIFERL and C. S. BARRETT, *J. Appl. Cryst.* **2** (1969) 30.
8. P. V. GROTH, "Strukturbericht" (Akademische Verlagsgesellschaft, Leipzig, 1931) Vol. I, p. 25.
9. W. G. CADY, "Piezoelectricity" (McGraw-Hill Book Co. Inc., New York, 1966), p. 23.
10. "International Tables for Crystallography" (Kynoch Press, Birmingham, 1952) Vol. I.
11. J. W. TESTER, Ph.D. Thesis, Massachusetts Institute of Technology (1971) p. 229.

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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° (for As) from the X-ray beam and $\{100\}_{rh}$ (psuedo three-fold) lying 18° (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 (1 1 1) 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 $\{100\}_{fcr}$ planes (in Miller indices referred to the face centred rhombohedral cell) exhibit pseudo-fourfold symmetry and the normals to the $\{\bar{1}11\}_{fcr}$ 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