

The Young's modulus and Poisson's ratio of arsenic, antimony and bismuth

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The orientational dependences of the Young's modulus and Poisson's ratio of the A7 structure elements arsenic, antimony, and bismuth are investigated, using available experimental data of the six elastic compliance constants. The behaviour of these technical elastic constants in antimony and bismuth is shown to differ not only in degree but also in kind from that of arsenic, which exhibits the characteristics expected of a layer-like crystal; arsenic is elastically a very anisotropic material, its Young's modulus varies by a factor as large as 11.3: the largest anisotropy ratio reported for a metallic element.

1. Introduction

A study of the anisotropy of the elastic behaviour of the group VB semimetals arsenic, antimony, bismuth is continued here by a comparison between their Poisson's ratios and Young's moduli. In general, details of Poisson's ratio in crystalline solids are sparse. These elements constitute a unique series by virtue of their rhombohedral A7 structure of space group D_{3d}^5 ($R\bar{3}m$). The crystal lattice is comprised of two interpenetrating face-centred rhombohedra. The trigonal (z) axis, formed by the intersection of three mirror planes mutually oriented at $\pm 120^\circ$, lies along the long body diagonal of the primitive unit cell defined from the lattice translation vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. Three options are open for the bisectrix (y) axis; the chosen y -axis is defined by projecting an \mathbf{a}_i onto the trigonal plane; the positive y -direction is then taken as outwards from the origin 0 of the \mathbf{a}_i (see Fig. 1 of [1]). A positive binary (x) axis then completes the right-handed set. The signs of the components of many tensors depend upon the definition of a right-handed axial set in the crystal being studied; for example, the signs of the magnetoresistivity tensor components [2, 3] and of C_{14} [1, 4, 5], and the orientation dependence of the Umkehr effect [6, 7] depend upon this assignment.

An interesting feature is that while its symmetry is identical to that of bismuth (rhombohedral angle $\alpha = 57^\circ 19'$) and antimony ($\alpha = 57^\circ 14'$), the crystal lattice of arsenic ($\alpha = 54^\circ 10'$) is much more distorted and tends towards a layer like structure; planes normal to

the trigonal (z) direction occur in pairs and binding between these successive double layers is weak [1, 8]. A grossly oversimplified but useful model for arsenic, in which tightly-bound double layers are assumed to be held together by van der Waals forces, gives the correct magnitude for the z -axis linear compressibility and the thermal expansion [1]. Recently, as part of a study of the anisotropy of elastic behaviour, the orientation dependence of elastic wave propagation in arsenic, antimony and bismuth [8], and also in Bi_2Te_3 and $\text{Bi}_{1.6}\text{Sb}_{0.4}\text{Te}_3$ [9], has been compiled and contrasted. In layer-like crystals vibrations are excited preferentially in the directions of greatest linear compressibility because these have lower frequencies. All these materials, but arsenic much more strongly than the others, exhibit the characteristics of layer-like crystals: high, direction-insensitive velocities of waves transmitted within the tightly-bound layers and smaller velocities along the direction (z) of weakest binding.

To obtain a clearer physical insight into the elastic properties of crystals than is provided by the six elastic stiffness constants, the conventional elastic moduli have to be considered. These describe the deformation of the crystals under static loads. Previously Pace, Saunders and Sümengen [1] have examined the effects of hydrostatic pressure; arsenic is the least compressible of the elements as far as bulk dilation is concerned, but is the most readily compressed along the z -axis. This property is understandable on the basis of the weak interlayer binding of

arsenic. A further physical appreciation can be achieved by comparing and contrasting the Poisson's ratios and Young's moduli of these elements. In spite of the great importance of these parameters little work is available on their anisotropy in materials of moderately low symmetry; Crocker and Singleton [10] have detailed the orientation dependences of the Young's and the shear moduli in mercury - another material belonging to the $\bar{3}m$ point group. Recently, Turley and Sines [11] have discussed methods for obtaining the directional behaviour of Young's modulus, the shear modulus and Poisson's ratio in cubic crystals. It is essentially their trigonometric method for determining Poisson's ratio that has been extended here to obtain numerical values for this parameter in the group V elements.

2. Procedure for Calculation of Poisson's ratio and Young's modulus

The generalized form of Hookes' Law is

$$\epsilon_{ij} = S_{ijkl} \sigma_{kl} \tag{1}$$

where ϵ_{ij} and σ_{kl} are the strain and stress tensors respectively. For trigonal crystals belonging to the Laue group RI, which includes the point group of interest here, the elastic compliance tensor S_{ijkl} can be written in matrix notation (replacing subscripts 11 by 1, 22 by 2, 33 by 3, 23 and 32 by 4, 13 and 31 by 5, and 12 and 21 by 6) as

$$\begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} & 0 & 0 \\ S_{12} & S_{11} & S_{13} & -S_{14} & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ S_{14} & -S_{14} & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & S_{14} \\ 0 & 0 & 0 & 0 & S_{14} & S_{66} \end{pmatrix} \tag{2}$$

where S_{66} is equal to $2(S_{11} - S_{12})$.

Poisson's ratio relates lateral strain to longitudinal strain resulting from a longitudinal stress which is, from Equation 1,

$$\epsilon_{jj}/\epsilon_{ii} = S_{jiii} \sigma_{ii}/S_{iiii} \sigma_{ii} = S_{jiii}/S_{iiii} \tag{3}$$

For an isotropic material longitudinal extension is always accompanied by lateral contraction, so that Poisson's ratio is defined as $-S_{jiii}/S_{iiii}$ so as to give practical values which are greater than zero for such materials. However, in single crystals Poisson's ratio has values which depend on the directions of the stress and strain, and both positive and negative values can be found. For an arbitrary set of axes, Poisson's ratio (ν_{ij}) can

be written as $-S_{ijij}/S_{iiii}$, using the fact that S_{ijkl} equals S_{klij} . To calculate ν_{ij} the tensor transformation law is used to obtain the primed compliances.

$$S_{ijkl}' = a_{im} a_{jn} a_{kp} a_{lq} S_{mnop} \tag{4}$$

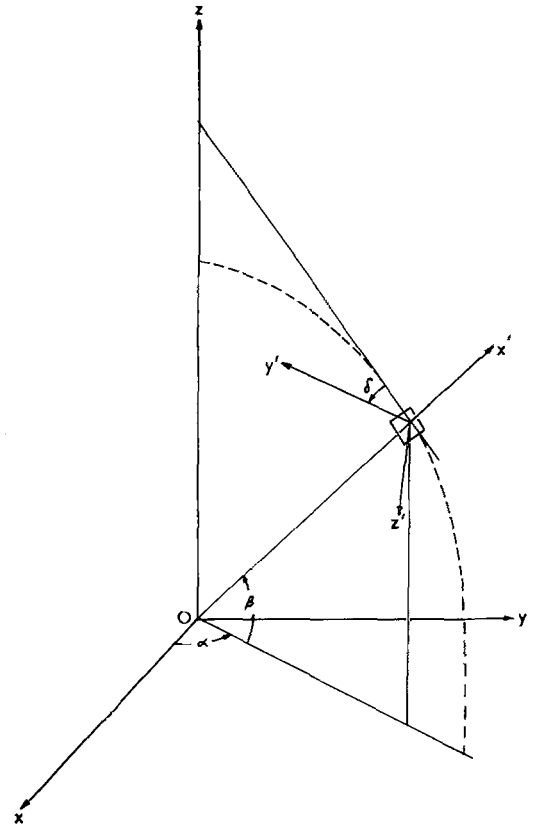


Figure 1 General transformation of axes. $0x'$ is defined by α and β . The direction of y' in the plane perpendicular to x' is defined by the angle δ between y' and the meridional tangent drawn perpendicular to x' and lying in the $x'z'$ -plane.

Let the x' -axis be in the direction of the applied stress. Then y' and z' will be in the plane perpendicular to $0x'$. If ν_{12}' is considered, it is then necessary to evaluate $-S_{12}'/S_{11}'$ (using the contracted subscript notation) for various orientations of y' in its plane. Note that S_{11}' has a constant value for a given direction of applied stress. The method outlined by Turley and Sines [11] has been used to calculate direction cosines, relative to the crystal axes, of the y' -axis as a function of the angle it makes with the meridional

tangent for the plane. Using the angles as defined in Fig. 1 the direction cosines are:

$$[\mathbf{a}_{ij}] = \begin{bmatrix} & \text{A} & & \text{B} & & \text{C} \\ \text{D} \cos \delta - \text{E} \sin \delta & & \text{F} \cos \delta - \text{G} \sin \delta & & \text{H} \cos \delta \\ \text{D} \sin \delta + \text{E} \cos \delta & & \text{F} \sin \delta + \text{G} \cos \delta & & \text{H} \sin \delta \end{bmatrix} \quad (5)$$

where

$$\begin{aligned} \text{A} &= \cos \alpha \cos \beta & \text{E} &= -\sin \alpha \\ \text{B} &= \sin \alpha \cos \beta & \text{F} &= -\sin \alpha \sin \beta \\ \text{C} &= \sin \beta & \text{G} &= \cos \alpha \\ \text{D} &= -\cos \alpha \sin \beta & \text{H} &= \sin \beta \end{aligned}$$

Substitution of values obtained from Equation 5 into Equation 4 leads to the desired result. Equations for S_{11}' and S_{12}' for trigonal symmetry are given:

$$S_{11}' = \mathbf{a}_{11}^4 S_{11} + \mathbf{a}_{11}^2 \mathbf{a}_{12}^2 (2S_{12} + S_{66}) + \mathbf{a}_{13}^4 S_{33} + \mathbf{a}_{13}^2 (1 - \mathbf{a}_{13}^2) (2S_{13} + S_{44}) + 2\mathbf{a}_{12} \mathbf{a}_{13} (3\mathbf{a}_{11}^2 - \mathbf{a}_{12}^2) S_{14} \quad (6a)$$

$$S_{12}' = (\mathbf{a}_{11}^2 \mathbf{a}_{21}^2 + \mathbf{a}_{12}^2 \mathbf{a}_{22}^2) S_{11} + (\mathbf{a}_{21}^2 \mathbf{a}_{12}^2 + \mathbf{a}_{11}^2 \mathbf{a}_{22}^2) S_{12} + [\mathbf{a}_{23}^2 (\mathbf{a}_{11}^2 + \mathbf{a}_{12}^2) + \mathbf{a}_{13}^2 (\mathbf{a}_{21}^2 + \mathbf{a}_{22}^2)] S_{13} + [2\mathbf{a}_{21} \mathbf{a}_{11} (\mathbf{a}_{23} \mathbf{a}_{12} + \mathbf{a}_{13} \mathbf{a}_{22}) + \mathbf{a}_{22} \mathbf{a}_{23} (\mathbf{a}_{11}^2 - \mathbf{a}_{12}^2) + \mathbf{a}_{12} \mathbf{a}_{13} (\mathbf{a}_{21}^2 - \mathbf{a}_{22}^2)] S_{14} + \mathbf{a}_{23}^2 \mathbf{a}_{13}^2 S_{33} + [\mathbf{a}_{13} \mathbf{a}_{23} (\mathbf{a}_{12} \mathbf{a}_{22} + \mathbf{a}_{11} \mathbf{a}_{21})] S_{44} + \mathbf{a}_{21} \mathbf{a}_{22} \mathbf{a}_{11} \mathbf{a}_{12} S_{66} \quad (6b)$$

The form of Equations 6a and b enables certain other primed coefficients to be calculated. For example, S_{22}' can be found by substituting \mathbf{a}_{21} , \mathbf{a}_{22} , \mathbf{a}_{23} for \mathbf{a}_{11} , \mathbf{a}_{12} , \mathbf{a}_{13} in the equation for S_{11}' , and so on. A computer programme has been prepared to perform these calculations as the angle δ varies from 0 to 360°, given values of \mathbf{a}_{11} , \mathbf{a}_{12} , \mathbf{a}_{13} (direction cosines of the applied stress direction) and of the unprimed compliances as the input data.

Young's modulus is the ratio of stress in some direction to the resulting strain in the same direction. If the applied stress is along the x -axis, then Young's modulus is given by $1/S_{1111}$. To find its value for any stress direction, it is necessary to evaluate $1/S_{1111}'$ from Equations 6a and b where \mathbf{a}_{11} , \mathbf{a}_{12} and \mathbf{a}_{13} define the direction of interest.

3. Results and Discussion

Calculations of Young's modulus and Poisson's ratio for arsenic, antimony and bismuth have been performed using the elastic compliance data reproduced in Table I. Unlike Young's modulus the Poisson's ratio cannot be represented by a surface because its value depends on both the

TABLE I Elastic compliance constants of arsenic, antimony and bismuth (10^{-12} cm² dyn⁻¹)

	Arsenic	Antimony	Bismuth
S_{11}	30.3	16.2	25.74
S_{12}	20.2	- 6.1	- 8.01
S_{13}	- 55.2	- 5.9	- 11.35
S_{14}	1.67	- 12.2	- 21.5
S_{33}	137.8	29.5	40.77
S_{44}	45.0	38.6	115.9
S_{66}	20.2	44.6	67.51
Reference	[1]	[5]	[4]

direction of the applied stress and on the strain direction in the plane normal to this. A convenient way of representing Poisson's ratio is to plot its angular dependence superimposed on a standard projection of the lattice so that it is centred on the point on the standard projection representing the direction of the applied stress. This is illustrated in Fig. 2 for arsenic, antimony and bismuth, in which the direction cosines for the point at the centre of each small diagram are given. Thus the points around the circumference of the semicircle ACB represent directions in the xy -plane; the point 0 at the circle centre is the trigonal (z) direction, points A and B' correspond to the $+y$ - and $-y$ -directions, respectively; the $+x$ -direction is represented by point C. Crystal symmetry considerations lead to an equivalence of A' with A, and B' with B, so that calculations done for any 120° sector of the standard projection suffice to give a complete description of Poisson's ratio in these crystals. Fig. 2 is drawn for 180°, however, in order to show more clearly the difference in form of the cross-sections obtained when the applied stress is in the yz -plane and making an angle of 45° with the $+y$ - and with the $-y$ -direction. Although the layout in Fig. 2 describes the general features of the anisotropy of Poisson's ratio for each element, to provide more readily accessible quantitative data for the parameter enlarged sections for each element are presented in Figs. 3, 4 and 5.

The effect of the layer-like nature of arsenic on its elastic behaviour can be clearly seen in Fig. 2a. The shape of each Poisson's ratio section is determined almost entirely by the angle that the applied stress direction makes with the z -axis. Thus when the stress is in the xy -plane, the shape is so similar for each that one diagram suffices (curve 1 of Fig. 3 which corresponds to A, F, B, C, A', F' and B' in Fig. 2a) to describe Poisson's

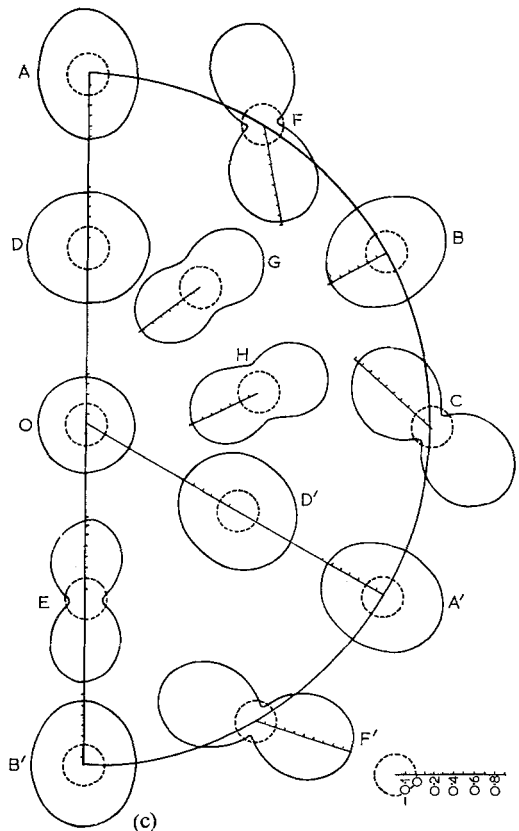
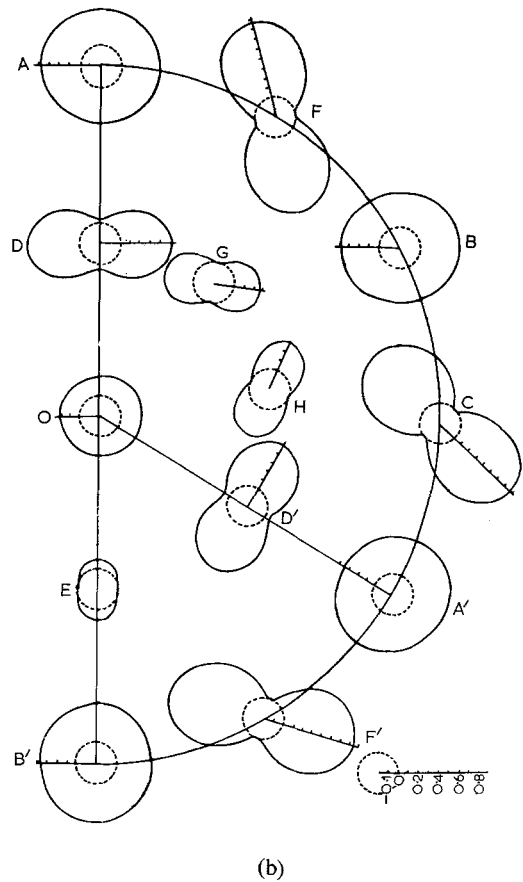
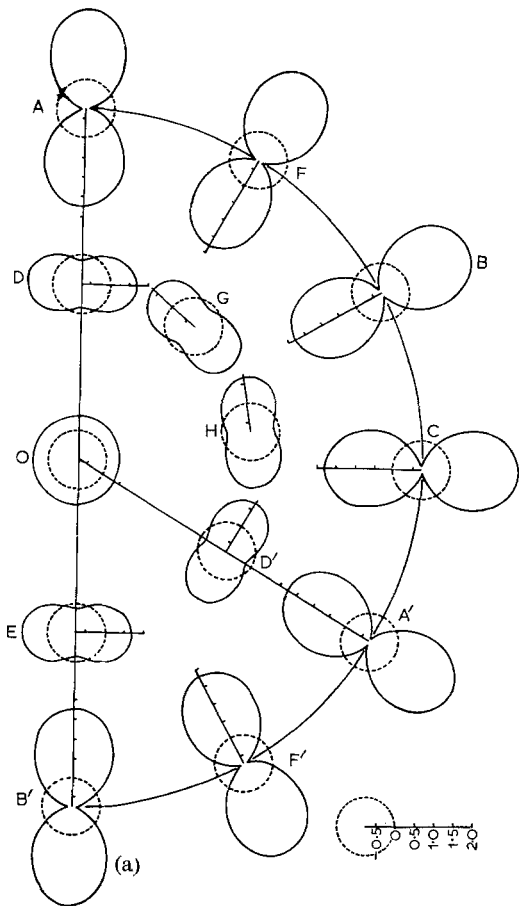


Figure 2 Directional dependence of Poisson's ratio for various directions of applied stress in (a) arsenic, (b) antimony and (c) bismuth. They are drawn on a standard projection on to the xy -plane. Direction cosines of the stress directions corresponding to the various curves are: A(0, 1, 0); A'(-0.866, 0.5, 0); B(0.5, 0.866, 0); B'(0, -1, 0); C(1, 0, 0); D(0, 0.707, 0.707); D'(0.612, -0.354, 0.707); E(0, -0.707, 0.707); F(0.866, 0.5, 0); F'(-0.5, 0.866, 0); G(0.455, 0.521, 0.707); H(0.696, 0.113, 0.707); O(0, 0, 1).

ratio: differences are within the error arising from that in the compliance constants used in the calculation. A similar cylindrical symmetry is found for angles other than 90° between the z -axis and the stress direction (curve 2 in Fig. 3 corresponds to D, G, H, D', E of Fig. 2a). It should, perhaps, be repeated that when considering the meaning of these curves a positive Poisson's ratio means a contraction as a result of a tensional stress whereas expansion occurs in directions where there is a negative value. Examples of the latter case are found in certain stress directions in arsenic and bismuth. The essential

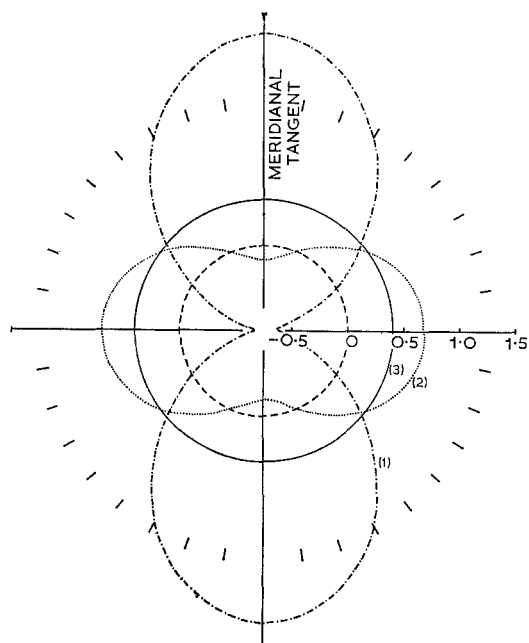


Figure 3 Detailed behaviour of Poisson's ratio for arsenic. Direction cosines of normal to each curve are — $(0, 0, 1)$; — · — · — $(n_1, n_2, 0)$; · · · · $(n_1, n_2, 1/\sqrt{2})$.

behaviour of arsenic under a stress applied in the xy -plane can be seen from curve 1 of Fig. 3. The lattice contracts along the z -axis (perpendicular to the layers) and expands in the appropriate perpendicular direction with strains of respectively 1.8 and 0.7 times the longitudinal one.

The Poisson's ratios of antimony and bismuth (see Figs. 2b and c, 4 and 5) differ in several respects from those in arsenic: the layer-like characteristics are much less evident, while for stresses at an angle to the z -axis the behaviour now depends much more on the x - and y -components (compare curves A and F in Fig. 2b and c). When compared with each other antimony and bismuth are seen to be quite similar, although the anisotropy in bismuth is rather greater than that in antimony. In both elements there is a marked difference between the behaviour under a stress applied in the $+y+z$ quadrant (D) and that in the $-y+z$ quadrant (E), as would be expected.

The dependence upon orientation of Young's modulus for the three elements is illustrated in Fig. 6a and b. The Young's modulus surface exhibits the inversion symmetry expected for materials of this point group. For a stress

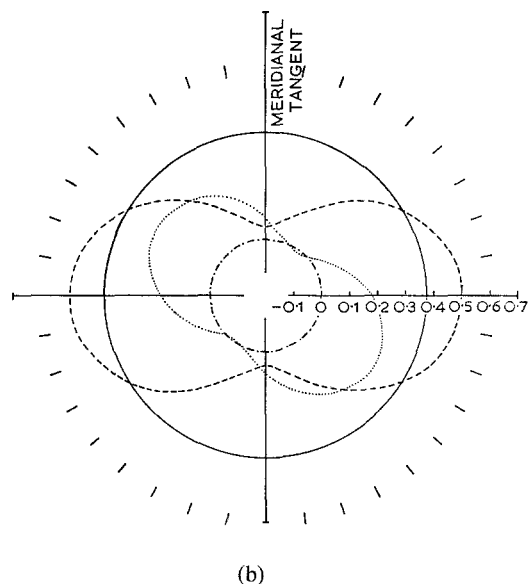
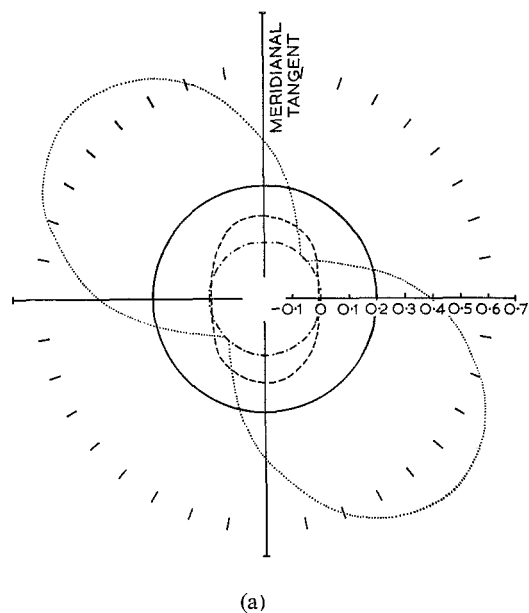


Figure 4 Detailed behaviour of Poisson's ratio for antimony. Direction cosine of normal to each curve are (a) — $(0, 0, 1)$; - - - $(0, -0.707, 0.707)$; · · · · $(0.5, 0.866, 0)$. (b) — $(0, 1, 0)$; - - - $(-0.707, 0.707, 0)$; · · · · $(0.696, 0.113, 0.707)$.

direction in the xy -plane, this modulus is independent of orientation and the computed values are for arsenic 3.30×10^{11} dyn cm^{-2} , for bismuth 3.89×10^{11} dyn cm^{-2} and for antimony

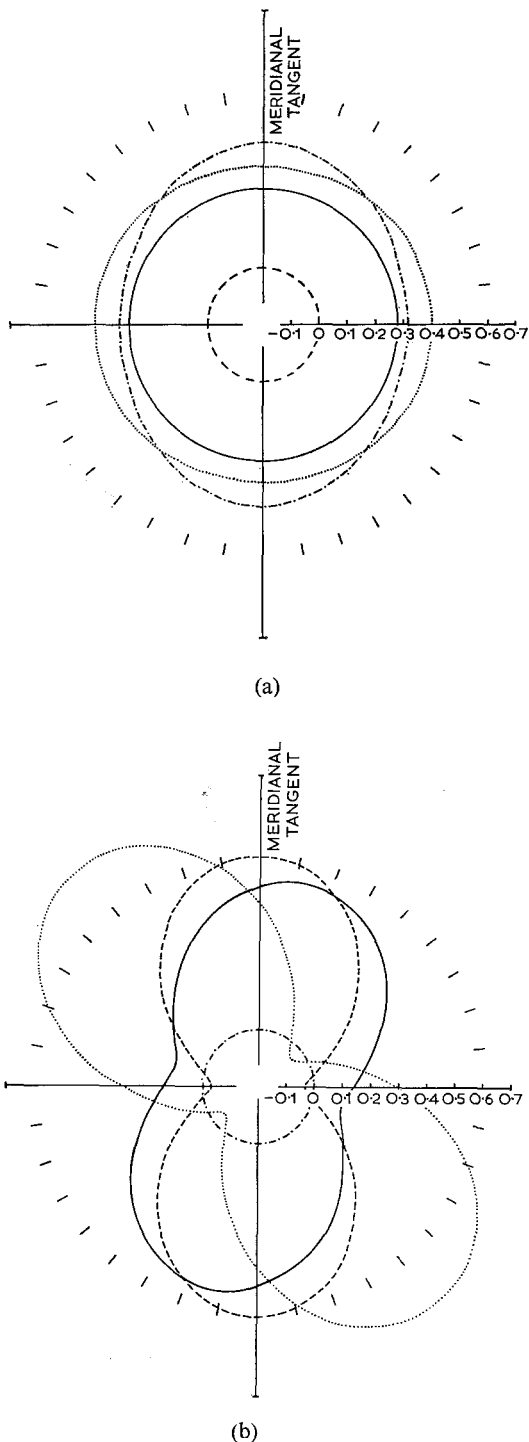
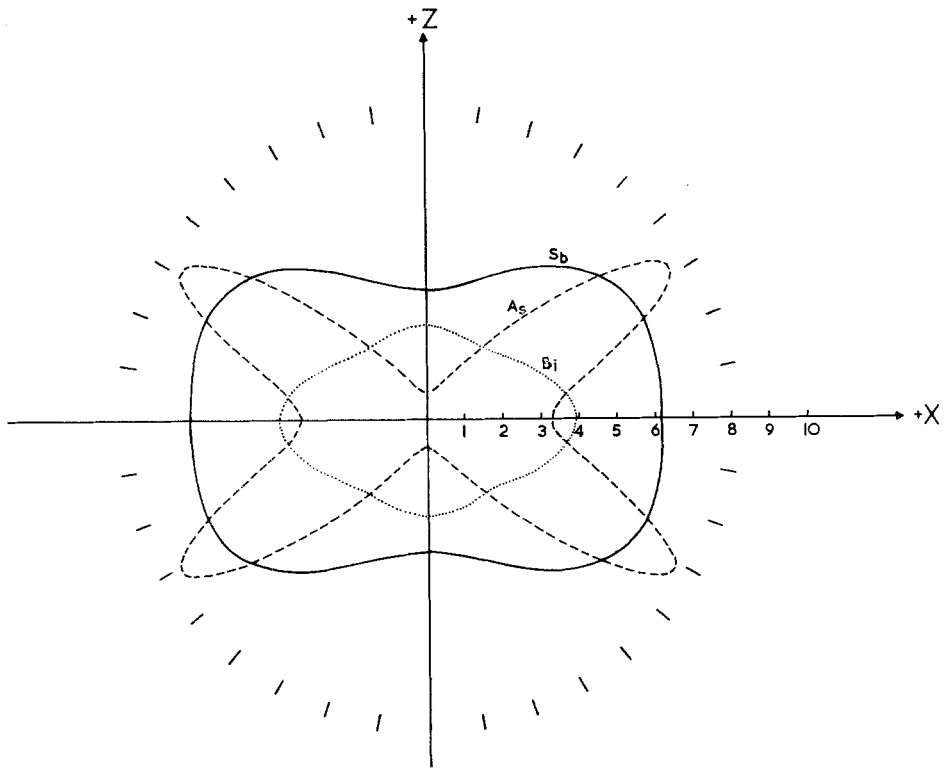


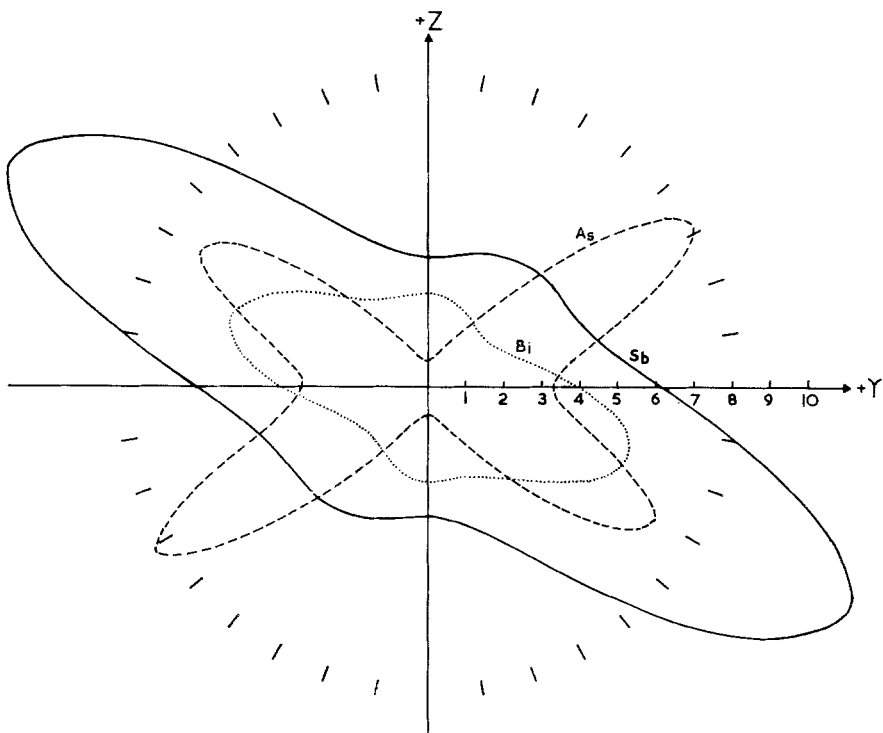
Figure 5 Detailed behaviour of Poisson's ratio for bismuth. Direction cosines of normal to each curve are (a) ——— (0, 0, 1); - - - - (0, 1, 0); ... (0, 0.707, 0.707). (b) ——— (0.455, 0.521, 0.707); - - - - (0, - 0.707, 0.707) ... (0.5, 0.866, 0).

6.17×10^{11} dyn cm^{-2} . The Young's modulus of arsenic shows the characteristics expected of a layer-like lattice with weak binding between the layer planes; the minimum value is 0.726×10^{11} dyn cm^{-2} for a stress applied along the direction (z) of weakest binding. The maximum value (8.18×10^{11} dyn cm^{-2}) lies in the $+y + z$ quadrant of the mirror plane at an angle of 31° from the $+y$ -axis; there is a second maximum (6.9×10^{11} dyn cm^{-2}) at 30° from the $-y$ -axis in the $-y + z$ quadrant. Arsenic is elastically a very anisotropic material with an anisotropy factor of 11.3, considerably greater than the ratio of 7.0 for mercury, previously quoted as the most anisotropic pure metallic material [10]. In antimony the Young's modulus behaviour is curious and demonstrates the importance of correct $(+x + y + z)$ axial assignment in these materials; the maximum value (12.5×10^{11} dyn cm^{-2}) lies in the mirror plane in the $-y + z$ quadrant at an angle of 62° from the $+z$ -axis, while the values in the $+y + z$ quadrant are much smaller; the minimum value (3.39×10^{11} dyn cm^{-2}) is that for a stress applied along the z -axis, and the anisotropy ratio is therefore 3.7, much less than that for arsenic but still large (see Table XIX, ref. [12]). The Young's modulus of bismuth is much less direction dependent (anisotropy factor 2.85) but now the minimum no longer occurs when a stress is applied along the z -axis but for one applied at 48.5° from the $+z$ -axis in the $+y + z$ quadrant. The maximum value of Young's modulus for this element is that for a stress along a direction 71° from the $+z$ -axis in the $-y + z$ quadrant.

To conclude, a method for computing the Poisson's ratio in anisotropic materials has been developed and applied in particular to the rhombohedral, A7 structure semimetals arsenic, antimony and bismuth of point group $\bar{3}m$. The directional dependence of Young's modulus, as well as the Poisson's ratio, has been investigated for these materials. Both these technical constants reflect strongly the layer-like nature, especially in the case of arsenic; thus the anisotropy of Poisson's ratio is large in planes normal to particular stress directions. The limits on Poisson's ratio of $+0.5$ and -1.0 , which follow from stability conditions for isotropic materials, do not apply for single crystals and values obtained range outside these figures. The Young's modulus surface cross-sections also evidence the great anisotropy of the A7 structure semimetals.



(a)



(b)

Figure 6 Cross-sections of the Young's modulus surface for arsenic, antimony and bismuth: (a) xz -plane; (b) yz -plane.

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