

Acta Cryst. (1962). **15**, 167

The Crystal Structures of the Germanium-Arsenic Compounds. I. Germanium Diarsenide, GeAs₂

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(Received 24 January 1961)

The crystal structure of GeAs₂ has been determined from Patterson projections and by direct methods. The orthorhombic unit cell has the dimensions

$$a_0 = 14.76, b_0 = 10.16, c_0 = 3.728 \text{ \AA}.$$

The space group is *Pbam*, and there are eight formula units of GeAs₂ per unit cell. Each Ge atom is bonded tetrahedrally to four As atoms, and each As atom forms three short bonds to Ge or As atoms and three long bonds to As atoms in a distorted octahedral arrangement. Viewed along the *c*-axis, groups of two Ge and three As atoms form columns of irregular puckered pentagons which are bonded together through a fourth As atom into layers parallel to (100). The long As-As bonds are, with one exception, between these layers.

Introduction

The phase diagram of the germanium-arsenic system (Stöhr & Klemm, 1940) shows two compounds, GeAs (m.p. 737 °C.) and GeAs₂ (m.p. 732 °C.). Schubert, Dörre & Günzel (1954) have reported GeAs to be monoclinic and GeAs₂ to be orthorhombic. Interest in the nature of the chemical bonding in these compounds and their properties as possible semiconducting materials has prompted the preparation of samples and the investigation of their crystal structures. The crystal structure of GeAs₂ is described here.

Experimental

Crystals of GeAs₂ were grown by heating germanium with a slight stoichiometric excess of arsenic in an evacuated sealed quartz tube to 800 °C., maintaining this temperature for about one hour, and then cooling slowly. A crystalline mass was obtained from which small individual crystals could be separated. The crystals are acicular with a grey metallic appearance and have well-developed, highly reflective faces. They are soft and bend easily. A perfect cleavage occurs parallel to the length of the crystals.

From rotation and equi-inclination Weissenberg photographs taken about the long dimension of the crystal, the following unit cell dimensions were obtained (λ of Cu *K* α = 1.5418 Å):

$$a_0 = 14.76 \pm 0.03, b_0 = 10.16 \pm 0.03, c_0 = 3.728 \pm 0.008 \text{ \AA}.$$

These values agree well with those reported by Schubert *et al.* (1954). The observed density reported by Stöhr & Klemm (1940) is 5.39 g.cm.⁻³, giving eight

formula units of GeAs₂ per unit cell. The calculated density is 5.284 g.cm.⁻³.

Measurements of crystals on an optical goniometer showed that the important prism forms are {100} and {210}, with {110} occurring occasionally. The usual shape of the crystals is that of laths elongated in the [001] direction and having (100) as the prominent face. The perfect cleavage is parallel to this face.

The space group extinctions observed were: *hkl* present in all orders; *h0l* present only with $h=2n$; and *0kl* present only with $k=2n$. These extinctions are permitted by the space groups *C*_{2v}^s-*Pba*2 and *D*_{2h}^s-*Pbam*. A careful comparison of the *hk0* and *hk2* Weissenberg photographs showed no significant difference between the intensities of corresponding reflections on the two photographs. The space group *Pbam* was therefore assumed.

The intensity data for the structure determination were measured visually from multiple-film equi-inclination Weissenberg photographs of the *hk0* and *hk1* reflections. There were 188 *hk0* and 182 *hk1* reflections observed. The *hk1* reflections were corrected for spot extension by the equation given by Phillips (1954). As the linear absorption coefficient of GeAs₂ for Cu *K* α radiation is 392 cm.⁻¹, it was necessary to correct the observed intensities for absorption. The crystal used to obtain the intensity data approximated a hexagon in cross section. The smallest dimension was 0.096 mm. between parallel (100) faces, and the largest dimension was 0.157 mm. between the intersections of pairs of parallel (110) and ($\bar{1}10$) faces. A somewhat idealized cross section of the crystal was divided into 40 equal areas, and the transmission factors were then calculated for the *hk0* and *hk1* reflections by the method described by Henshaw (1958).

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Table 1. *Final parameters*

	Atom	$ e_0 $	$ \partial^2 e/\partial x^2 $	$ \partial^2 e/\partial y^2 $	x	y	z	$\sigma(x)$	$\sigma(y)$
<i>hk0</i> data	Ge ₁	82.1	1270	1088	0.1381	0.4188	0.0000	0.0033 Å	0.0043 Å
	Ge ₂	79.2	1223	1224	0.2664	0.2015	0.5000	0.0034	0.0038
	As ₁	82.9	1295	1292	0.2958	0.3537	0.0000	0.0033	0.0036
	As ₂	85.5	1547	1520	0.0385	0.2262	0.0000	0.0027	0.0031
	As ₃	90.5	1533	1391	0.1117	0.1011	0.5000	0.0028	0.0034
	As ₄	89.5	1573	1290	0.4028	0.0631	0.5000	0.0027	0.0036
<i>hk1</i> data	Ge ₁	81.7	1346	1556	0.1374	0.4195	0.0000	0.0028	0.0026
	Ge ₂	80.2	1381	1507	0.2670	0.2033	0.5000	0.0028	0.0026
	As ₁	83.5	1533	1566	0.2948	0.3528	0.0000	0.0025	0.0026
	As ₂	85.8	1624	1317	0.0382	0.2257	0.0000	0.0023	0.0030
	As ₃	87.2	1478	1332	0.1118	0.1018	0.5000	0.0026	0.0030
	As ₄	85.3	1436	1438	0.4015	0.0625	0.5000	0.0026	0.0028

Determination of the structure

Since the expected interatomic distances in GeAs₂ are all about 2.4 Å or greater, the short c axis should insure that all atoms will project on (001) without any overlapping. In addition, if all atoms are in the mirror planes of *Pbam*, the *hk0* data and the *hk1* data will provide two independent structure determinations.

The mirror positions of this space group are four-fold, requiring the location of two germanium atoms and four arsenic atoms. There are two independent sets of equivalent mirror positions:

$$x, y, 0; \bar{x}, \bar{y}, 0; \frac{1}{2}+x, \frac{1}{2}-y, 0; \frac{1}{2}-x, \frac{1}{2}+y, 0;$$

$$x, y, \frac{1}{2}; \bar{x}, \bar{y}, \frac{1}{2}; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}.$$

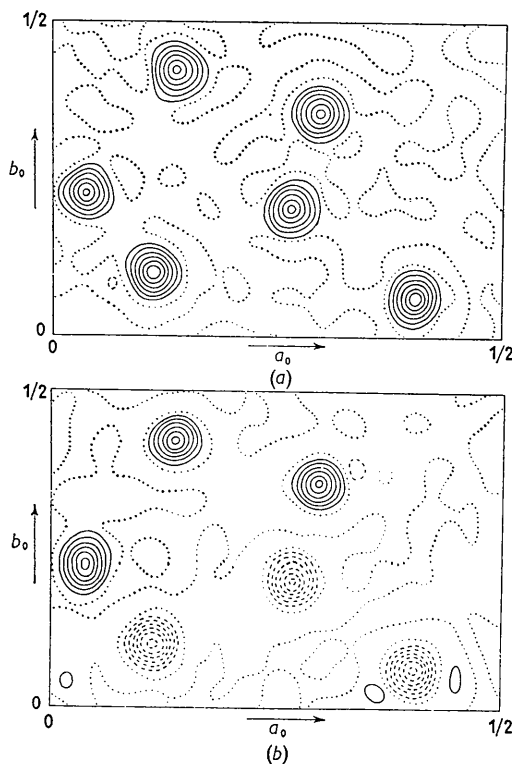


Fig. 1. Electron density projections for germanium diarsenide: (a) the *hk0* Fourier projection, and (b) the *hk1* generalized Fourier projection. The zero contour is dotted, and the negative contours are broken. The contour interval is arbitrary.

As an *h0l* precession photograph showed only even orders of $00l$, it was assumed that one germanium and two arsenic atoms occupied positions in each set. This was subsequently verified.

After correction of the intensities for absorption and the Lorentz and polarization factors, three Patterson projections were calculated: the first was calculated with the *hk0* data only; the other two, combining both *hk0* and *hk1* data, were composite Patterson projections. The second was calculated with terms of the type $|F(hk0)|^2 + |F(hk1)|^2$, and shows the interatomic vectors between atoms in the same mirror plane. The third was calculated with terms of the type $|F(hk0)|^2 - |F(hk1)|^2$, and shows the interatomic vectors between atoms in adjacent mirror planes. Little useful information was immediately obtainable from the first Patterson projection; however, it was possible

Table 2. *Interatomic distances and angles in germanium diarsenide*

Atoms	Multiplicity	Distance	σ
Ge ₁ -As ₁	1	2.420 Å	0.004 Å
As ₂	1	2.451	0.004
As ₄ '	2	2.440	0.003
Ge ₂ -As ₁	2	2.450	0.003
As ₃	1	2.506	0.004
As ₄	1	2.452	0.004
As ₂ -As ₃	2	2.500	0.003
As ₁ -As ₂ '	1	3.677	0.004
As ₃ '	2	3.422	0.004
As ₃ -As ₃ ''	1	3.891	0.004
As ₄ -As ₂ '	2	3.481	0.003
As ₄ '''	1	3.156	0.004

Atoms	Angle	Atoms	Angle
As ₁ -Ge ₁ -As ₂	110.7°	As ₃ -As ₂ -As ₁ ''	108.2°
As ₁ -Ge ₁ -As ₄ '	113.5	As ₁ ''-As ₂ -As ₄ ''	64.6
As ₂ -Ge ₁ -As ₄ '	109.5	As ₃ -As ₂ -As ₃	96.4
As ₄ '-Ge ₁ -As ₄ '	99.6	As ₄ ''-As ₂ -As ₄ ''	64.7
As ₁ -Ge ₂ -As ₃	114.4	Ge ₂ -As ₃ -As ₂	100.8
As ₂ -Ge ₂ -As ₄	102.8	Ge ₂ -As ₃ -As ₁ '	86.3
As ₃ -Ge ₂ -As ₄	120.5	As ₁ '-As ₃ -As ₃ ''	87.1
As ₁ -Ge ₂ -As ₁	99.1	As ₂ -As ₂ -As ₃ ''	84.3
Ge ₁ -As ₁ -As ₃ '	100.4	As ₂ -As ₃ -As ₂	96.4
Ge ₁ -As ₁ -Ge ₂	90.4	As ₁ '-As ₃ -As ₁ '	66.0
Ge ₂ -As ₁ -As ₂ '	91.8	Ge ₂ -As ₄ -Ge ₁	98.5
As ₂ -As ₁ -As ₃ '	76.7	Ge ₂ -As ₄ -As ₂ '	96.6
Ge ₂ -As ₁ -Ge ₂	99.1	As ₂ '-As ₄ -As ₄ '''	73.8
As ₃ -As ₁ -As ₃ '	66.0	Ge ₁ '-As ₄ -As ₄ '''	88.8
Ge ₁ -As ₂ -As ₃	98.4	Ge ₁ '-As ₄ -Ge ₁ '	99.6
Ge ₁ -As ₂ -As ₄	81.5	As ₂ '-As ₄ -As ₂ '	64.7

$hk0$ data on an absolute scale by the method of Wilson (1942) and calculating the unitary structure factors, it was found possible to derive 50 relations among the phases of the reflections. From these relations the phases of 30 reflections were obtained, 16 of which depended on the unknown phase of one reflection, (810). Two electron density projections were calculated with these data corresponding to the two possible phases of (810). Neither of these projections could be immediately interpreted in terms of a reasonable structure because of several extra peaks that were present. As an aid in deciding between the two Fourier projections, the minimum function of Buerger (1951, 1959) was applied to the $hk0$ Patterson projection. The three atoms previously located were used as the starting point with the vectors between pairs of atoms related by the nearest two-fold axis defining the minimum functions. The resulting minimum function map showed a pronounced resemblance to the 30-term Fourier projection for which the sign of $F(810)$ was negative. Knowing the positions of three atoms on this projection permitted the parameters of the remaining three atoms to be determined. The phases of two weak reflections used in this Fourier projection were found to be wrong in the final calculations.

These parameters were refined by Fourier methods, using the $hk0$ and hkl data independently. The final $hk0$ and hkl projections are shown in Fig. 1. The final parameters obtained from the $hk0$ and hkl data after correction for series-termination errors by the back-shift method of Booth (1946) are listed in Table 1. The standard deviations of the atomic coordinates were calculated by the method of Cruickshank (1949). The unweighted average of the two sets of parameters were used to calculate the interatomic distances and angles that are listed in Table 2. The observed and calculated structure amplitudes are given in Table 3. The scattering factors for these calculations were obtained by the analytical expression proposed by Vand, Eiland & Pepinsky (1957), using the constants given by them. The percentage discrepancy was 14.5 for the $hk0$ data and 16.5 for the hkl data. An isotropic temperature correction, $\exp[-B(\sin \theta/\lambda)^2]$, with $B = 0.21 \text{ \AA}^2$, was used in the final calculations. The quantitative agreement between the larger observed and calculated structure amplitudes is not as good as is usually obtained, although the agreement for the smaller values is generally good. In particular, the agreement for (121), the most intense reflection from this crystal as observed on a Debye-Scherrer powder

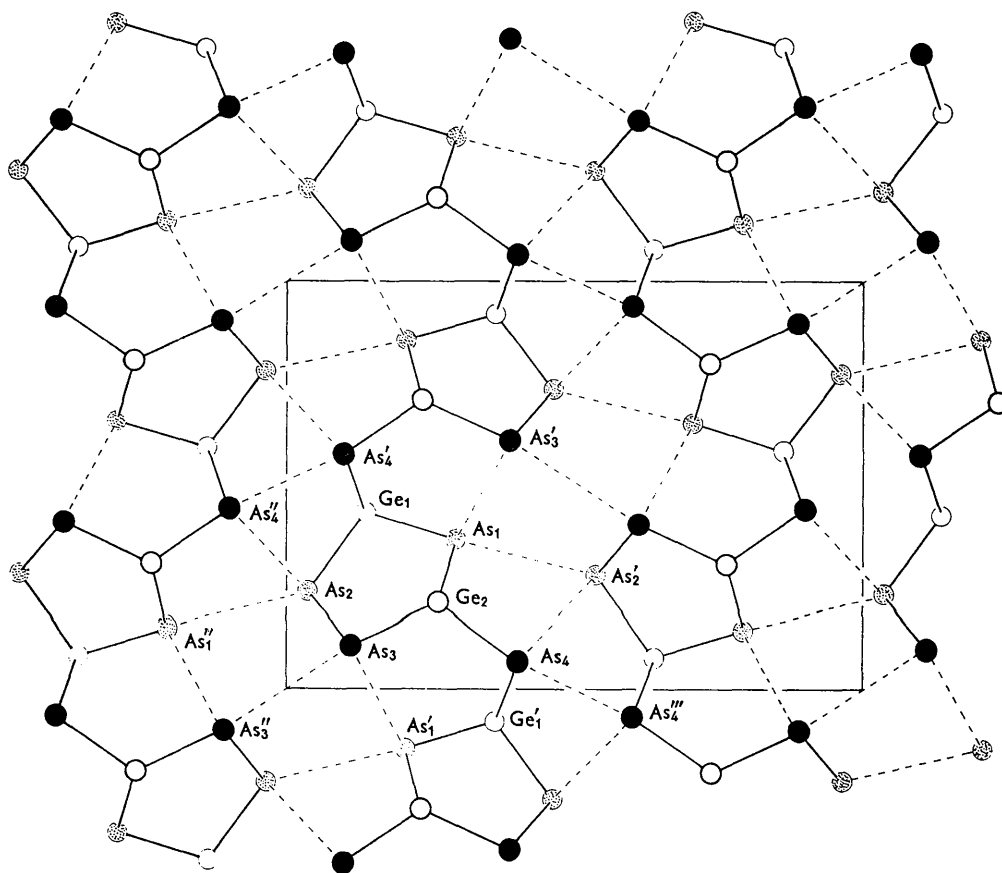


Fig. 2. Schematic drawing of the crystal structure of germanium diarsenide. The light circles are atoms at $z=0$, and the heavy circles are atoms at $z=\frac{1}{2}$. The shaded circles are the arsenic atoms. The solid lines represent normal covalent bonds, and the broken lines represent the weak inter-arsenic bonds. One unit cell is outlined.

photograph, is very poor. This is largely due to the difficulty of making accurate visual estimates of photographic intensities from a highly absorbing crystal. Extinction has undoubtedly also affected some of the more intense reflections.

Discussion

Fig. 2 is a schematic drawing of the crystal structure showing the numbering of the atoms. The identification of the germanium and arsenic atoms was made by consideration of the number of covalent bonds formed by each atom. From Table 2, the list of interatomic distances and angles, it is seen that the germanium atoms form four approximately tetrahedral covalent bonds to arsenic atoms, and the arsenic atoms form three pyramidal covalent bonds to germanium or arsenic atoms. The germanium-arsenic bond lengths range from 2.42 to 2.51 Å, with an average of 2.453 Å. This is not significantly different from the value of 2.43 Å calculated from Pauling's covalent bond radii (Pauling, 1960). The single arsenic-arsenic bond length is 2.50 Å, about the same as is found in metallic arsenic.

When viewed along the *c* axis, two germanium and three arsenic atoms make an irregular puckered pentagon. The bonds between Ge₂ and As₁ and between As₂ and As₃ form these pentagons into columns parallel to the *c* axis. The fourth arsenic atom then binds these columns together into layers parallel to (100).

In addition to three close neighbors, each arsenic atom has three more-distant arsenic neighbors arranged so that the coordination is roughly octahedral. These longer interatomic distances range from 3.16

to 3.89 Å. The shortest distance is about the same as found in metallic arsenic. The forces between these layers in GeAs₂ must therefore be considerably weaker than the forces between the layers in metallic arsenic. This is borne out by the great ease with which crystals of GeAs₂ may be cleaved parallel to (100). Four of these longer distances are between layers; the fifth, between As₁ and As₃, is within the layers.

I wish to thank Mrs Mary Frances Harvey for her assistance in making many of the calculations, particularly the absorption corrections, Mr H. I. Fleischer of the Computing Services Section for his help in seeing the numerous crystallographic calculations through the IBM 709 computer, and Dr Richard E. Marsh of the California Institute of Technology for preparing a precession photograph of a GeAs₂ crystal.

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Short Communication

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1961). **15**, 171

The crystal structure of biuret hydrate. A correction. By E. W. HUGHES and H. L. YAKEL, *California Institute of Technology, Pasadena 4, California, U.S.A.* and H. C. FREEMAN, *University of Sydney, Sydney, Australia*

(Received 26 September 1961)

The paper of the above title (Hughes, Yakel & Freeman, 1961) bears an erroneous date of reception. It was received 15 June 1959, and not, as stated, 2 July 1960.

Reference

- HUGHES, E. W., YAKEL, H. L. & FREEMAN, H. C. (1961). *Acta Cryst.* **14**, 345.