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Precise Lattice Constants of Germanium, Aluminum, Gallium Arsenide, Uranium, Sulphur, Quartz and Sapphire

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The lattice constants of germanium, aluminum, gallium arsenide, α-uranium, orthorhombic sulphur, natural quartz and synthetic sapphire have been determined to six significant figures by a precision single crystal X-ray method. A comparison is made with previously determined values for these materials.

Introduction

The lattice constants of many materials reported in the literature have been determined by powder diffraction methods. This technique has some inherent difficulties; for example, individual particles in a powder sample are not necessarily single crystals. Strains produced in these particles during preparation cannot easily be eliminated, even by annealing. Further, for non-cubic materials, different expansion coefficients in different crystallographic directions may produce additional strains. These strains broaden the lines of diffraction patterns, leading to decreased accuracy in the measurements.

Today, very pure and perfect single crystals of many substances can be grown. A method for accurate lattice constant determination using single crystals has been developed by Bond (1960). Some of the errors encountered in other methods have been eliminated. For the rest, corrections can be accurately computed. The lattice constants of a number of single crystals have been measured and are given here for seven pure materials.

Sample preparation

Each specimen for X-ray examination was prepared by cutting a piece about $\frac{1}{8}'' \times \frac{1}{8}'' \times \frac{1}{4}''$ from a single crystal of the material, having one surface parallel to the plane to be measured. This was accomplished by mounting the crystal in plaster of paris in an adjustable holder, accurately orienting it by X-ray diffraction, and cutting it with a diamond saw. Then the crystal was etched until any strained material produced by the cutting was removed, as determined by the sharpness of the X-ray reflection.

Since aluminum and sulphur are too soft to be cut in this way, other methods were found for these specimens. The aluminum crystal was cut with a string saw and a solution of cupric chloride. Flat surfaces on the sulphur crystals were obtained by gentle lapping with cotton tape moistened in toluene and backed by a strip of bakelite. By these means strain-free surfaces within a few minutes of being parallel to the desired crystal planes can be prepared.

The sapphire crystal was small enough as grown to be mounted in the apparatus, and its natural faces were used.

Sample purity

The germanium crystal was grown in a vacuum by a floating zone method by E. Buehler of Bell Telephone Laboratories, Incorporated. Its carrier ion concentration, a measure of purity, is 1×10^{13} cm.$^{-3}$. Gallium arsenide was also prepared by the floating zone method (Whelan & Wheatley, 1958) and has a carrier ion concentration of 1×10^{17} cm.$^{-3}$. The aluminum crystal was grown by P. H. Schmidt of Bell Telephone Laboratories, Incorporated, from zone-refined aluminum by a modified Bridgman method, starting with 99·9997% pure aluminum obtained from United Mineral and Chemical Corporation, New York.

The single crystal of uranium was obtained from M. H. Mueller and E. S. Fisher of Argonne National Laboratory. It was prepared by a grain coarsening technique (Fisher, 1957) from uranium metal containing 0·007 to 0·01% impurities, chiefly carbon. It was electropolished just before measurement in a phosphoric acid, alcohol, and ethylene glycol electrolyte to remove any oxide film.

The sulphur crystals were obtained from J. Kalnajs of MIT who grew them from a toluene solution from sulphur originally presented by R. Fanelli, Texas Gulf Sulphur Company, New York, to Bass (1953) for optical absorption studies.

Quartz specimens were cut from a crystal of natural Brazilian quartz. The sapphire crystal, grown by J. P. Remeika of Bell Telephone Laboratories, Incorporated, consists of $Al_2O_3 + 0{\cdot}008\%$ chromium. Spectrographic analysis shows the presence of any other transition elements in only slight trace amounts.

Method

The lattice constants of each material were measured at room temperature by the precision X-ray method of W. L. Bond, which has previously been described in detail (Bond, 1960). This method consists of the accurate determination of the angle between two positions of the crystal when X-rays are being diffracted from the desired crystal planes. The crystal was mounted on the crystal-carrying shaft and oriented, using a special orienting device, so that the desired planes were accurately parallel to the shaft axis. This shaft was clamped in a divided circle which reads directly to one second of arc. Water pumped through a surrounding insulating jacket maintained the temperature within 0·1 °C.

A set of four measurements of the Bragg angle, θ, was made for each plane, the crystal shaft being turned 90° and reclamped in the divided circle between measurements. The mean of these four θ values was used to calculate p', the lattice parameter. The wave-

Table 1. *Computation of the lattice constants of germanium, aluminum, and gallium arsenide*

Material	Ge	Al	GaAs
hkl	711	333	551
X-radiation	Cu $K\alpha_1$	Cu $K\alpha_1$	Cu $K\alpha_1$
λ (kX.)	1·537395	1·537395	1·537395
θ_1	76° 28′ 55″	81° 14′ 35″	76° 39′ 36″
θ_2	76° 28′ 52″	81° 14′ 30″	76° 39′ 40″
θ_3	76° 28′ 54″	81° 14′ 25″	76° 39′ 39″
θ_4	76° 28′ 52″	81° 14′ 25″	76° 39′ 41″
θ (mean)	76° 28′ 53·3″ ± 1·5″	81° 14′ 28·8″ ± 4·8″	76° 39′ 39·0″ ± 2·2″
Lp corr.	0·5″	4·2″	0·5″
a'	5·646022	4·041386	5·641803
δ	$16{\cdot}1 \times 10^{-6}$	$8{\cdot}3 \times 10^{-6}$	$15{\cdot}0 \times 10^{-6}$
Refr. corr.	0·000096	0·000035	0·000089
Axial div.	0·000015	0·000011	0·000015
a (kX.)	5·646133	4·041432	5·641907
Std. dev.	± 0·000010	± 0·000015	± 0·000014
Temp. (°C.)	24·6	24·8	24·7

Table 2. *Computation of the lattice constants of α-uranium*

hkl	400	060	006
X-radiation	Cu K_β	Co $K\alpha_1$	Cu $K\alpha_1$
λ (kX.)	1·38935	1·78529	1·537395
θ_1	77° 21′ 45″	66° 6′ 51″	68° 51′ 2″
θ_2	77° 21′ 8″	66° 6′ 45″	68° 51′ 2″
θ_3	77° 21′ 25″	66° 6′ 50″	68° 51′ 4″
θ_4	77° 21′ 22″	66° 6′ 56″	68° 51′ 16″
θ (mean)	77° 21′ 25″ ± 15″	66° 6′ 50·5″ ± 4·5″	68° 51′ 6·0″ ± 6·7″
Lp corr.	8″	0·2″	0·2″
p' (parameter)	$a' = 2{\cdot}847726$	$b' = 5{\cdot}857550$	$c' = 4{\cdot}945249$
δ	$38{\cdot}4 \times 10^{-6}$	$63{\cdot}5 \times 10^{-6}$	$47{\cdot}0 \times 10^{-6}$
Refr. corr.	0·000115	0·000444	0·000267
Axial div.	0·000007	0·000015	0·000013
p (kX.)	$a = 2{\cdot}847848$	$b = 5{\cdot}858009$	$c = 4{\cdot}945529$
Std. dev.	± 0·000046	± 0·000057	± 0·000062
Temp. (°C.)	24·6	24·6	24·6

Table 3. *Computation of the lattice constants of orthorhombic sulphur*

hkl	12,0,0	0,16,0	0,0,24
X-radiation	Cu $K\alpha_1$	Cu $K\alpha_1$	Co $K\alpha_1$
λ (kX.)	1·537395	1·537395	1·78529
θ_1	62° 2′ 20″	73° 18′ 39″	61° 14′ 54″
θ_2	62° 2′ 24″	73° 18′ 46″	61° 14′ 46 ′
θ_3	62° 2′ 28″	73° 18′ 45″	61° 14′ 51″
θ_4	62° 2″ 24″	73° 18′ 35″	61° 14′ 55″
θ (mean)	62° 2′ 24·0″ ± 3·3″	73° 18′ 41·3″ ± 5·2″	61° 14′ 51·5″ ± 4·0″
Lp corr.	0·1″	0·4″	0·1″
p' (parameter)	$a' = 10{\cdot}44337$	$b' = 12{\cdot}83997$	$c' = 24{\cdot}43630$
δ	$6{\cdot}6 \times 10^{-6}$	$6{\cdot}6 \times 10^{-6}$	$9{\cdot}0 \times 10^{-6}$
Refr. corr.	0·00009	0·00009	0·00029
Axial div.	0·00003	0·00003	0·00006
p (kX.)	$a = 10{\cdot}44349$	$b = 12{\cdot}84009$	$c = 24{\cdot}43665$
Std. dev.	± 0·00009	± 0·00010	± 0·00026
Temp. (°C.)	24·8	24·8	24·8

length of radiation and the diffracting plane were chosen to give the highest possible value of θ, which increases the precision of the results. Corrections were applied for Lorentz and polarization factors, axial divergence of the beam, and refraction. The refraction correction is given by

$$p=p'(1+\delta/\sin^2\theta)$$[*]

in which

$$\delta=ne^2\lambda^2/2\pi mc^2,$$

where n is the number of electrons per cm.^{3}, e is the charge on the electron, m is its mass, c is the velocity of light and λ is the wavelength of the radiation used.

These corrections were added to p' to give p, the final value of the lattice constant. The standard deviation for each parameter was computed from the variation in measured θ.

Tables 1–5 give a summary of the data and the computation of the lattice parameters for each material.

Table 4. *Computation of the lattice constants of natural quartz*

hk·l X-radiation	33·0 Cu $K\alpha_1$	00·6 Cu $K\alpha_1$
λ (kX.)	1·537395	1·537395
θ_1	70° 9′ 30″	58° 46′ 8″
θ_2	70° 9′ 30″	58° 46′ 5″
θ_3	70° 9′ 30″	58° 46′ 8″
θ_4	70° 9′ 32″	58° 46′ 4″
θ (mean)	70° 9′ 30·5″ ± 1·0″	58° 46′ 6·3″ ± 2·1″
Lp corr.	0·2″	0·1″
p' (parameter)	$a'=4{\cdot}903266$	$c'=5{\cdot}393873$
δ	$8{\cdot}6\times10^{-6}$	$8{\cdot}6\times10^{-6}$
Refr. corr.	0·000048	0·000064
Axial div.	0·000013	0·000014
p (kX.)	$a=4{\cdot}903327$	$c=5{\cdot}393951$
Std. dev.	±0·000009	±0·000033
Temp. (°C.)	24·8	24·6

Table 5. *Computation of the lattice constants of sapphire*

hk·l X-radiation	40·8 Cu $K\alpha_1$	00·12 Fe $K\alpha_1$
λ (kX.)	1·537395	1·932076
θ_1	62° 17′ 43″	63° 24′ 21″
θ_2	62° 17′ 42″	63° 24′ 10″
θ_3	62° 17′ 44″	63° 24′ 18″
θ_4	62° 17′ 39″	63° 24′ 4″
θ (mean)	62° 17′ 42·0″ ± 2·2″	63° 24′ 13·3″ ± 7·7″
Lp corr.	0·1″	0·1″
p' (parameter)	$a'=4{\cdot}749344$[*]	$c'=12{\cdot}964295$
δ	$12{\cdot}5\times10^{-6}$	$19{\cdot}8\times10^{-6}$
Refr. corr.	0·000076	0·000322
Axial div.	0·000012	0·000034
p (kX.)	$a=4{\cdot}749432$	$c=12{\cdot}964651$
Std. dev.	±0·000027	±0·000242
Temp (°C.)	24·7	24·7

[*] The value measured for c was used in the equation for computing a.

Discussion

Comparison of the present measurements with previously reported values is made in Tables 6–10.

X-ray wavelengths, from the original measurement by Siegbahn of the cleavage spacing of calcite, are given in kX. units, based on a former value of Avogadro's number. New values of Avogadro's number alter the value of the kX. unit slightly. Since the relative values of X-ray wavelengths are known more accurately than absolute values, the kX. unit is used in this work. Many lattice constant values in the literature are expressed in Ångström units, and these have been converted to kX. units for comparison by dividing by 1·00202.

A temperature correction has not been included in these data, as the expansion coefficients are not known as accurately as the lattice spacings. However, since this correction would involve only the fifth decimal place, it does not affect the comparison with other reported values. In the case of aluminum, its large coefficient of expansion does influence the comparison, as will be mentioned below. The literature values were assumed to be at room temperature (25 °C.) unless otherwise noted.

There have been many measurements of the lattice constant of aluminum, as it is often used to demonstrate the technique or precision of a new X-ray

Table 6. *Comparison of the reported values of the lattice constant of aluminum*

Investigation	*a*	Temp.
von Göler & Sachs (1929)	4·0402 kX.	—
Wassermann (1930)	4·0404	—
Owen & Iball (1932)	4·0406 ± 0·0003	room
Jette & Foote (1935)	4·04139 ± 0·00008	25 °C.
Ievinš & Straumanis (1936)	4·04145 ± 0·00002	25
van Bergen (1941)	4·04091 ± 0·00006	20
Lu & Chang (1941)	4·0411 ± 0·0001	20
Wilson (1941)	4·0413$_4$ ± 0·0001	25
Axon & Hume-Rothery (1948)	4·0413$_4$	25
Ellwood & Silcock (1948)	4·0409 ± 0·0002	18
Owen, Liu & Morris (1948)	4·0406	18
Hume-Rothery & Boultbee (1949)	4·04142	25
Straumanis (1949)	4·04145 ± 0·00002	25
Poole & Axon (1952)	4·0412$_1$	25
Hill & Axon (1953)	4·0411$_8$	25
Swanson & Tatge (1953*a*)	4·0405	25
Smakula & Kalnajs (1955)	4·04142	25
Figgins, Jones & Riley (1956)	4·04150 ± 0·00002	25·5
This work	4·04143 ± 0·00002	24·8

Table 7. *Comparison of the reported values of the lattice constant of germanium*

Investigation	*a*	Temp.
Goldschmidt (1927)	5·647 ± 0·006 kX.	room
Nitka (1937)	5·648 ± 0·004	20 °C.
Greiner (1952)	5·6461 ± 0·0001	25
Straumanis & Aka (1952)	5·64607 ± 0·00004	20
Swanson & Tatge (1953*b*)	5·6462	26
This work	5·64613 ± 0·00001	24·6

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[*] This was erroneously reported as sin 2θ in equation (7) of a previous publication (Bond, 1960).

method. With increased purity of samples and better temperature control, increased precision has been obtained. Table 6 contains the results of nineteen investigations. When a temperature correction is applied to the values obtained at lower temperatures, there is good agreement to four decimal places.

Table 8. *Comparison of the reported values of the lattice constant of* GaAs

Investigation	a
Kolm, Kulin & Averback (1957)	5·6446 kX.
Giesecke & Pfister (1958)	5·6420 ±0·0002 (at 18°)
Lublin (1961)	5·6416 ±0·0002
This work	5·64191 ±0·00001

There are few reported lattice constants for germanium or gallium arsenide, as pure material has only recently become available. Table 7 shows the agreement among recent measurements of germanium. Table 8 lists a few values for gallium arsenide.

A number of papers have been published concerning the expansion coefficients of uranium. The lattice constants of Bridge, Schwartz & Vaughan (1956) and of Konobeevsky *et al.* (1958) listed in Table 9 have been computed at 25 °C. from their equations for expansion. These are compared with other values measured at 25 °C. Differences between measurements are probably due to impurities, as pure uranium is difficult to obtain.

Since a comparison of the lattice constants of sulphur has recently been published (Cooper, Bond & Abrahams, 1961), it has not been included in the tables given here. The present values are in good agreement with those given by previous investigators.

Many measurements of the lattice constants of quartz have been made, since it has commonly been used to calibrate X-ray cameras. However, Keith (1950) showed that different specimens gave different values, probably due to the presence of impurities. This has been confirmed by Afaras'eva, Kamentsev & Frank-Kamenetskii (1959) who measured ten natural specimens from different parts of the Soviet Union. They found that an increase in measured impurity content produced an increase in the volume of the quartz cell. Cohen & Sumner (1958) also give a correlation of lattice constants and impurities and conclude that interstitial impurities cause expansion of the a axis and substitutional impurities expand both axes. Table 10 lists a number of values of the lattice constants of natural quartz. The variations just discussed are evident. The variation with impurity content seems to be the same for synthetic quartz so far investigated, but not included here.

A similar difficulty in comparing measurements of sapphire exists, because the lattice constants would vary depending on the concentration of impurities. Only one previous reference was found. Shiroda & Amano (1950) measured the lattice constants of artificial sapphire at 31 °C. and found $a = 4{\cdot}7532$ and $c = 12{\cdot}9819$ kX.

Conclusion

As can be seen in the above tables, the present values agree well with previous measurements, and in addition extend the precision to six significant figures. This is an improvement for all the materials except aluminum, for which a number of values including six figures have already been reported. The precision of these measurements is a few parts per million for

Table 9. *Comparison of the reported values of the lattice constants of α-uranium*

Investigation	a	b	c
Jacob & Warren (1937)	2·852 kX.	5·865 kX.	4·945 kX.
Bridge, Schwartz & Vaughan (1956)	$2{\cdot}848_2$	$5{\cdot}855_8$	$4{\cdot}946_1$
Konobeevsky *et al.* (1958)	$2{\cdot}847_9$	$5{\cdot}854_4$	$4{\cdot}945_6$
Chiotti, Klepfer & White (1959)	$2{\cdot}847_7$	$5{\cdot}853_0$	$4{\cdot}944_3$
Sturcken & Post (1960)	2·848 ±0·001	5·857 ±0·001	4·945 ±0·001
Mueller (1954)	2·8483 ±0·0003	5·8573 ±0·0015	4·9463 ±0·0004
This work	2·84785 ±0·00005	5·85801 ±0·00006	4·94553 ±0·00006

Table 10. *Comparison of the reported values of the lattice constants of natural quartz*

Investigation	a	c	Temp.
Bradley & Jay (1933)	4·9029 kX.	5·3933 kX.	18 °C.
Wilson & Lipson (1941)	$4{\cdot}903_2$	$5{\cdot}393_7$	18
Keith (1950)	4·90309 ±0·00005	5·39367 ±0·00005	25
Cohen & Sumner (1958)	4·9032 to 4·9042 ±0·0002	5·3938 to 5·3943 ±0·0002	25
Afaras'eva *et al.* (1959)	4·9022 to 4·9038 ±0·0002	5·3922 to 5·3942 ±0·0002	18
This work	4·90333 ±0·00001	5·39395 ±0·00003	25

all the materials except sulphur and uranium. Their precision is about 1 part in 10^5, probably due to slight strains in the crystals.

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