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Lattice Parameters, Coefficients of Thermal Expansion, and Atomic Weights of Purest Silicon and Germanium*

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Lattice parameter determinations of 99.97 percent pure silicon (containing 0.03 percent carbon) were carried out using the asymmetric method, a 64-mm precision camera in a thermostat at constant temperatures (10, 20, 30, 40, and 50°C). The powder mounts, about 0.12-mm in diameter, were translated and rotated during the exposure. Only the (444)-CuK α_1 line was used for the determinations. The lattice parameter $a = 5.41991 \pm 0.00003 kX$ (5.43086Å) at 20°C, corrected for refraction, was obtained; the linear lattice expansion coefficient (between 10 and 50°C) was 4.15×10^{-6} , the density at 20°C was 2.32831 ± 0.00031 g/cm³ (determined by the suspension method), and the atomic weight was 28.083 ± 0.013 (in agreement with the new chemical weight 28.09) showing that the silicon crystals used, under certain limitations, were sound although the possibility of interstitial atoms is not excluded.

The lattice parameter of purest germanium (99.99 and 99.999 percent) was measured by the same method using the (422)-CrK α_1 and α_2 lines: $a_{20} = 5.64607 \pm 0.00004 kX$ (5.65748Å) for both materials. The expansion coefficients were $\alpha = 6.65 \times 10^{-6}$ and 5.92×10^{-6} , respectively. The density was 5.3234 ± 0.0025 g/cm³ at 25°C and the calculated atomic weight 72.593 ± 0.037 in agreement with the present chemical weight 72.60. Thus, germanium crystals are sound; however, interstitial atoms are possible.

The precision of lattice parameter determination was about 1:200,000, but in the case of 99.999 percent germanium the precision was considerably better. This shows again that lattice constant determinations can be performed with highest precision and without use of any extrapolation method. The method of lattice parameter determination applied is an absolute one.

INTRODUCTION

SILICON and germanium were selected for the investigation because of the following reasons: (1) although these elements were known for a long time, it is only recently that they were obtained in a very pure form, and, therefore, the lattice parameters, expansion coefficients, and the degree of perfection of silicon and germanium crystals were not exactly known; and (2) the two elements are gaining increasing attention which may be attributed to the variability, diversity, and peculiarity of many of their properties, especially of germanium,¹ which have been studied very little until recent years.

The data available in the literature concerning the lattice parameter of silicon, and especially of germanium, are rather limited and to a certain extent, unreliable, because of the relatively impure materials used (99.8–99.9 percent). The best results attained concerning the constants of both elements (being cubic and of diamond type of structure) are given in Table I.

The expansion coefficient of germanium at room temperature is not even known. Table I shows that the revision of the values of lattice parameters, expansion coefficients, and densities with highest purity materials is, therefore, justified.

I. THE MATERIAL USED

The hyper-pure silicon was received from Dr. C. M. Olson of du Pont Company and used both for x-ray investigations and density determinations. It was pre-

pared by Lyon, Olson, and Lewis,² who reduced silicon tetrachloride by zinc vapor at 950°C. The silicon thus obtained consisted of metallic gray crystals which were practically free from metallic impurities (not over 0.001 percent) and had an extremely low electrical conductivity ($0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°). However, the silicon contained small amounts of carbon (about 0.03 percent). Thus, the element was about 99.97 percent pure.

Two samples of germanium obtained from Mr. E. J. Ritchie of the Eagle-Picher Company (Joplin, Missouri) of the purity 99.99 and better than 99.999 percent were investigated. The spectrographic analysis of the last germanium sample was given in a private communication with Mr. Ritchie, as follows (in percent by weight):

Ca—0.00024	Cu—0.000047
Mg—0.00005	Si—0.00002.

This purity was reported to be in agreement with the electrical properties observed by the producers of the particular slug.

The germanium samples were in the form of small ingots with strong optical reflection of silvery color.

Small quantities of each of the metals were ground in an agate mortar and the x-ray mounts were made from the resulting powder. Since the material was brittle, the grinding was effected so easily that no sieving and annealing of the resulting powder was necessary before the preparation of the powder specimens. The x-ray pictures obtained were sharp enough to attain the highest precision.

II. EXPERIMENTAL PROCEDURE

Determination of Lattice Parameters

The exact values of the lattice parameters of silicon and germanium were determined at ten-degree intervals

* Extract from a thesis submitted by E. Z. Aka in partial fulfillment of the requirements for the Ph.D. degree at the Graduate School of the University of Missouri. The article was presented to the Eighth Annual Pittsburgh Conference on X-ray and Electron Diffraction (November 3, 1950).

¹ W. C. Dunlap, Jr., Gen. Elec. Research Lab. Rept. 1595.

² Lyon, Olson, and Lewis, J. Electrochem. Soc. **96**, 359 (1949).

between 10 and 50°C, using the following equipment: (1) a precise camera 64 mm in diameter, (2) a jacket into which the camera fitted and in which a constant temperature ($\pm 0.02^\circ\text{C}$) could be maintained by a circulating bath system, and (3) a comparator accurate to 0.001 mm for measuring the films 18 cm in length.³ Bare films could be inserted into the camera in the asymmetric position; this arrangement permits the computation of the exact Bragg angles without knowledge of the camera radius, without use of a standard substance, and without any corrections for film shrinkage. The powder mounts, 0.12 mm in diameter were thin enough and quite transparent to x-rays so that the absorption correction could be neglected.³ Sharpest and most uniform lines were obtained when the mounts were almost perfectly centered by means of a sample holder, which was rotated and simultaneously scanned over a range of 3 mm in the inside of the camera.⁴ The 6 cm long pinholes (collimators) had a bore of 0.5 or 0.8 mm. The lines were measured from peak to peak intensity. The patterns were indexed by a graphical method.⁵

Copper radiation ($\lambda K\alpha_1 = 1.537395kX$) was selected for production of asymmetric powder patterns of silicon at all temperatures (exposure 1 hour). Only the last $\alpha_1(444)$ line with $\vartheta \cong 80^\circ$ was used for the calculation of lattice constants because the $\alpha_2(444)$ line was superimposed by the $\beta(731)$ line, and hence was too broad to allow accurate measurements.

The germanium powder yielded, with chromium radiation the α_1 and $\alpha_2(422)$ lines under $\vartheta \cong 83^\circ$ ($\lambda K\alpha_1 = 2.28503kX$, $\lambda K\alpha_2 = 2.28891kX$). This doublet was clearly resolved, and the lines were strong and uniform if the samples were rotated and scanned for the twenty minutes of exposure. Both of these last lines were measured and used for the calculation of lattice constants.

Two sets of lines in the front reflection region, namely, $\alpha(111)$ and $\beta(111)$ were also measured on each of the silicon and germanium films for calculation of effective circumferences of the films and the factors of conversion.³

Density Determination

The density of silicon was determined by two methods: by the powder method of Baker and Martin⁶ based on Archimedes principle, and by the suspension method⁷ using single silicon crystals. Both methods were modified in order to make them more convenient for work.

The following distinguishing operations were performed in the density determination of silicon (in g/cm^3)

TABLE I. Lattice parameter a and linear expansion coefficient α of Si and Ge.

		a in kX	$^\circ\text{C}$	α in deg $\text{C}^{-1} \times 10^6$
v. Arkel ^a	Si	5.418	—	—
Jette, Foote ^b	Si	5.4198 ± 0.00034	25	—
Neuburger ^c	Si	5.4173 ± 0.0005	20	—
Fizeau ^d	Si	—	40	7.63
Erfiling ^e	Si	—	20–50	2.42
				0–20
Goldschmidt ^f	Ge	5.647	—	—
Nitka ^g	Ge	5.648	20	6.0 at 290°

- ^a A. E. v. Arkel, *Z. Krist.* **67**, 235 (1928).
^b E. R. Jette and F. Foote, *J. Chem. Phys.* **3**, 605 (1935).
^c M. C. Neuburger, *Z. Krist.* **92**, 313 (1935).
^d H. Fizeau, *Compt. rend.* **68**, 1125 (1869).
^e H. D. Erfiling, *Ann. Physik* **41**, 471 (1942).
^f V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente VIII," *Skrifter Norske Videnskaps-Akad. Oslo. I. Mat.-Natur. Kl.*, (1927).
^g H. Nitka, *Physik. Z.* **38**, 896 (1937).

at a certain temperature by the first method: (1) Purest benzene was added to the powdered silicon, and the powder-liquid mixture was outgassed as well as possible by the application of a suitable vacuum while magnetically stirring the mixture. (2) The first weighing was done while the powdered material, together with its container, was completely immersed in the benzene at a temperature measured. (3) The benzene in the container of the powdered material was evaporated completely after the first weighing. (4) The second weighing of the dry silicon powder was made in air. The first and the second weighings may be repeated by adding a little liquid medium (the same or different) to the dry powder in the container and proceeding as forementioned. The other weighings did not differ from the usual practice. The density was computed by a formula derived from that of Baker and Martin.⁶ The precision of the method is $\pm 5 \times 10^{-3} \text{ g}/\text{cm}^3$.

The density of silicon crystals was checked by the suspension method, since the values shown by the powder method are usually lower than they are actually. For this purpose a pycnometer of a special design was used. It was filled (over the mark) with a bromoform-ethanol solution of such composition that the silicon crystal or fragment, which was in the liquid, became suspended in it at a certain temperature. The temperature could be exactly controlled because the pycnometer was placed into a water bath. At the suspension temperature the liquid in excess was removed (down to the mark), and the pycnometer with the liquid and crystal was weighed. Knowing the volume of the pycnometer at the suspension temperature, the density of the liquid, which was equal to the density of the crystal, could be easily computed.

Single, well-developed crystals of silicon with bright, shiny planes were chosen for the determinations. They were 2–5 mm in length, 0.2–0.5 mm in diameter, and their weight was between 0.23–3.85 mg. It was impossible to inspect the crystals as to the presence of cracks or gaps because of the opaqueness of silicon. The crystals were treated with alcohol and some of them with

³ M. E. Straumanis, *J. Appl. Phys.* **20**, 726 (1949).

⁴ M. E. Straumanis and E. Z. Aka, *Rev. Sci. Instr.* **22**, 843 (1951).

⁵ M. E. Straumanis, *Am. Mineral.* (to be published).

⁶ I. Baker and G. Martin, *Ind. Eng. Chem. Anal. Ed.* **15**, 279 (1943).

⁷ H. L. Johnston and C. A. Hutchison, *J. Chem. Phys.* **8**, 870 (1940). D. A. Hutchison, *Phys. Rev.* **66**, 144 (1944).

TABLE II. Variation of lattice parameter of 99.97 percent pure silicon with temperature: φ —(444) α_1 back reflection angle, Cu-radiation.

Temp. in °C	φ in degrees	Parameter in kX	Parameter a_v
10.0	10.683	5.41962	5.41966
10.0	87	69	
10.0	86	67	
20.0	10.689	5.41973	5.41984
20.0	706	2003	
20.0	690	1975	
30.0	10.708	5.42007	5.42009
30.0	12	14	
30.0	07	05	
40.0	10.720	5.42028	5.42029
40.0	20	28	
40.0	22	32	
50.0	10.737	5.42059	5.42056
50.0	34	53	
50.0	36	57	

hydrofluoric acid. No heat treatment was applied as the formation of the crystals, according to the manufacturers, occurred at 950°C.²

The precision of this density determination method is not as high as the method of D. A. Hutchison ($\sim \pm 4 \times 10^{-6}$ g/cm³)⁷ but is at least $\pm 3 \times 10^{-4}$ g/cm³ which is sufficient in order to answer questions concerning the soundness of crystals. Besides, one density determination can be performed in three hours and all operations are simple. The reliability of the method was checked by the determination of density of sublimed sodium chloride crystals.

III. EXPERIMENTAL RESULTS

Lattice Parameters and Expansion Coefficients of Silicon and Germanium

The purpose of Table II is to show (1) the values of the lattice parameters of silicon obtained at different temperatures, (2) the variations in the values at one constant temperature, and (3) the method of attack. At every temperature three photographs were made.

TABLE III. Lattice parameter a of 99.97 percent pure silicon reduced to 20, 18, and 25°C ($\alpha = 4.15 \times 10^{-6}$).

Temp. °C	a_{Av} in kX	a reduced to 20°
10.0	5.41966	5.41989
20.0	5.41984	4
30.0	5.42009	7
40.0	5.42029	4
50.0	5.42056	9
	Average	5.41987 kX
	Corrected for refraction ^a	5.41991 \pm 0.00003 or 5.43086A
	At 18°C	5.41987 5.43082
	25°	5.42002 5.43097

^a Correction for refraction: P. P. Ewald in W. Wien and F. Harms, *Handbuch der Experimentalphysik* XXIV/2, 94, 116 (1930).

From these data the average lattice expansion coefficient between 10° and 50° was computed, assuming that in this interval the expansion is linear: $\alpha = 4.15 \times 10^{-6}$. This value lies between the coefficients obtained by Fizeau and Erling (Table I). By means of $\alpha = 4.15 \times 10^{-6}$ the average parameters of Table II were reduced to standard temperatures of 18, 20, and 25°C.⁸ (Table III).

The error given represents the maximum deviation from the average value and the precision of determination is close to 1:200,000.

In Table IV the lattice parameters obtained with 99.99 percent germanium are reported. Since the value of the parameter at 20°C was slightly too high (see Table V), the results were checked using 99.999 percent germanium. The average constants of all these measurements are shown in Table IV.

From these data the expansion coefficients were computed. It was obtained as an average value for 99.99 percent Ge— $\alpha = 6.65 \times 10^{-6}$ and for the purest metal— $\alpha = 5.92 \times 10^{-6}$. In Table V are recorded the lattice parameters of these two kinds of germanium, reduced to the three standard temperatures.

TABLE IV. Lattice parameter a of 99.99 and of 99.999 percent pure germanium at different temperatures. Average values of measurements of 3 and 2 films, respectively. Cr $K\alpha_1$ and α_2 radiation, plane 422. Accuracy of temperature readings: $\pm 0.02^\circ\text{C}$.

Temp. in °C	a in kX of	
	99.99 percent	99.999 percent Ge
10.0	5.64547	5.645518
20.0	5.64589	—
30.0	5.64618	5.646185
40.0	5.64657	—
50.0	5.64699	5.646856

Table V shows that the precision of determination of 99.99 percent germanium is about the same as in the case of silicon. The precision was lowered because of the results at 20°, which for some unknown reason became too high. An unusually high reproducibility was attained in the case of 99.999 percent germanium which gave sharper lines than the first sample. Further work will show whether it will be possible to reproduce this high precision (better than 1:2,000,000) or not.

Density and Atomic Weight of Silicon and Germanium

The atomic weight A_x of silicon and germanium was calculated using Avogadro's number:⁹

$$A_x = kN_s v d / n. \quad (1)$$

v is the volume of the unit cell (in kX^3), d —the density (g/cm³), n —the number of atoms per unit cell, N_s —

⁸ M. Straumanis and A. Ievins, *Z. anorg. u. allgem. Chem.* 238, 175 (1938).

⁹ M. E. Straumanis, *Acta Cryst.* 2, 82 (1949); *Z. Physik* 126, 49 (1949).

TABLE V. Lattice parameter a in kX of 99.99 and 99.999 percent pure germanium reduced to 20, 18, and 25°C. ($\alpha = 6.65 \times 10^{-6}$ and 5.92×10^{-6} , respectively.)

Temp. in °C	99.99 percent		99.999 percent	
	a_{Av}	a red. to 20°C	a_{Av}	a red. to 20°C
10.0	5.64547	5.64585	5.645518	5.645852
20.0	589	9	—	—
30.0	618	1	5.646185	51
40.0	657	2	—	—
50.0	699	6	5.646856	54
	Av.	5.64585		5.645852
	Ref. corr.	22		216
		5.64607 ± 0.00004 kX		5.646068 ± 0.000002 kX
	or	5.65748A		5.657473A
	At 18°C	5.64599 kX		5.646002 kX or 5.657407A
	25°	5.64627 kX		5.646235 5.657640

Siegbahn's Avogadro number,¹⁰ and k is a constant factor equal to 1.0002.^{9,11}

The relative error by which the atomic weights from x-ray and density data is affected, was calculated from the next Eq. (2) which is derived by logarithmic differentiation of Eq. (1), and elimination of v :

$$\Delta A_x/A = 3\Delta a/a + \Delta k/k + \Delta d/d. \quad (2)$$

N_s and n are constants.

In Table VI are reported the densities of silicon determined by the Baker and Martin⁶ method. Since the accuracy of determination is only $\pm 5 \times 10^{-3}$ and since there is a tendency to get lower results with the methods using powder, single silicon crystals were used for density determination with the suspension method. The measurements revealed that the crystals have densities which differ appreciably from each other, and the computed atomic weight of silicon showed for most of the determinations a considerably larger value than 28.06, its present atomic weight. Only three crystals out of twelve had lower values. One of these values, some of the middle values, the largest atomic weight, and the average value of 16 determinations (8 crystals) showing an $A_x \geq 28.07$, are summarized in Table VI.

The density of germanium was determined by Mr. Ritchie of the Eagle-Picher Company, using the Baker-Martin method.⁶ Five samples of purest germanium (three prepared from Tri-State ore and two from African ore) had a density 5.3234 ± 0.0025 g/cm³ at 25.0°C. The atomic weight computed, and the observed and calculated errors (Eq. (2)) are shown in Table VI.

IV. DISCUSSION

Soundness of Silicon and Germanium Crystals

The present value for the lattice constant of 99.97 percent pure silicon is about 2×10^{-4} unit higher than that one determined by Jette and Foote (see reference b in Table I); the agreement is still within the error limits given by them, although the silicon of Jette and Foote was of 99.84 percent purity.

No such comparison can be made in the case of germanium, because the only values for germanium available in the literature (Table I) are not of sufficient precision. The same is true concerning the linear lattice expansion coefficient of this element. (See reference g in Table I.)

The precision attained is about 1:200,000 while in the case of purest germanium it is considerably better. There might be some doubt concerning the high precision attained with a small camera, 64 mm in diameter. However, it was recently proven by Keith¹² that the 64-cm camera works as well as a large 19-cm "Unican" camera.

The data for the density of silicon given in the literature differ considerably¹³ because of the difference in purity of the samples. But also in the case of 99.97 percent silicon, there are differences in the densities of single silicon crystals which exceed the error limits of the method of determination (see Table VI). It is believed that these differences are due to two reasons; the presence of carbon (0.03 percent) and of microscopic cracks in the crystals. As silicon carbide that

TABLE VI. Densities and atomic weights of silicon and germanium. p —powder, c —crystal.

		d_t g/cm ³	t °C	d_{20° g/cm ³	A_x	A_{chem}^a	Diff.	$\pm \Delta A_x$
Si+0.03% C	p	2.326	20.0	...	28.055	28.09	-0.035	0.14 ^b
Si+0.03% C	c	2.3240	28.58	2.32426	28.034	28.09	-0.056	0.012
Si+0.03% C	{ c	2.32635	25.34	2.32651	28.0612	28.09	-0.029	0.0045 ^c
Si+0.03% C		2.32539	25.42	2.32649	28.0610			
Si+0.03% C		2.32629	28.33	2.32653	28.0615			
Si+0.03% C		2.32764	25.83	2.32781	28.075			
Si+0.03% C	c	2.32764	25.83	2.32781	28.075	...	-0.015	0.012
Si+0.03% C	c	2.32997	28.73	2.33022	28.106	28.09	+0.016	0.012
Av. of 8 Si ^d	c	2.32831	28.083	28.09	-0.007	0.012
Ge 99.999%	p	5.3234	25.0	...	72.593	72.60	-0.007	0.037

^a New atomic weight of silicon, see Chem. Eng. News 29, 4077 (1951).

^b Assuming that $\Delta a/a = 3 \times 10^{-5}$, $\Delta k/k = 5 \times 10^{-5}$ and $\Delta d/d = 5 \times 10^{-5}$ (Eq. (2)).

^c Highest precision attained with the same crystal: here $\Delta d/d = 2 \times 10^{-4}$.

^d All 8 showing an atomic weight $A_x \geq 28.07$.

¹⁰ M. Siegbahn, *Spektroskopie der Röntgenstrahlen* (Verlag. Julius Springer, Berlin, Germany, 1931), 2 Aufl., p. 43.

¹¹ M. Straumanis, *Z. Physik*, 126, 62 (1949).

¹² H. D. Keith, *Proc. Phys. Soc.* LXIII, 1034 (1950).

¹³ International Critical Tables, Vol. III, p. 29 (1928).

might have been formed during the preparation has a higher density (3.17 g/cm^3) than silicon itself, it might have influenced the density of the resulting product. However, the degree of this influence would also depend on the solubility of the silicon carbide in silicon, of which very little is known.¹⁴

Usually, the presence of microscopic cracks lowers the density of crystals. Therefore, crystals with fewer cracks will have a larger density, and for the silicon of such crystals a more correct x-ray atomic weight will be obtained. Eight crystals out of twelve had the highest densities observed, which corresponded to the atomic weight of 28.085 for silicon within the limit of ± 0.015 . Hence, the x-ray atomic weight was calculated only from the densities of these 8 crystals. An average value of 28.083 ± 0.013 was obtained. This value agrees within the error limits ($\pm 0.012 - 0.013$) with the new chemical atomic weight of silicon 28.09 recommended by the International Commission of Atomic Weights in September, 1951. Thus, silicon crystals are either sound (the difference -0.007 , Table VI, is within the error limits), or they may contain silicon carbide inclusions. The possibility of interstitial atoms in silicon⁹ can be discussed only after the investigation of a purer material. But it seems very probable that there are no vacant sites in silicon.

Purest germanium has an x-ray atomic weight which agrees within the error limits (Table VI) with its present

chemical atomic weight. But as the densities of a substance determined by its powder are in the most cases slightly too low, the x-ray atomic weight might be higher than the present chemical atomic weight. Thus, germanium crystals are sound, or they contain interstitial atoms. It seems that there is no possibility of vacant sites in germanium.

The objection can be made that the lattice parameters of both elements are too high because no corrections, except that one for refraction, were applied, and besides the Eq. (1) for atomic weight contains a factor $k > 1$. However, the introduction of the correction for absorption, which is negligibly small in the high back reflection region, would shift the lattice parameters to higher values, which would emphasize still more the possibility of interstitial atoms in silicon and germanium. The necessity of the factor k (Eq. (1)) has been proven already in an earlier work,⁹ and recently it was shown that also in the case of diamond,¹⁵ in order to get the right atomic weight for carbon, this factor is indispensable.

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¹⁴ A. E. van Arkel, *Reine Metalle* (Verlag J. Springer, Berlin, Germany, 1939), p. 478; H. von Wartenberg, *Z. anorg., u. allgem. Chem.* **265**, 186 (1951).

¹⁵ M. E. Straumanis and E. Z. Aka, *J. Am. Chem. Soc.* **73**, 5643 (1951).