

## Precision Density Determination of Large Single Crystals by Hydrostatic Weighing\*

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In connection with a study of crystal imperfections, the density of Si, quartz,  $\text{CaF}_2$ , CsI, Ge, TlCl, TlBr, and polycrystalline Al have been determined by an hydrostatic weighing method using ethylene bromide as the immersion liquid. Random and systematic errors have been discussed and the present accuracy of the order of  $10^{-5}$  reached.

### INTRODUCTION

DENSITY combined with lattice constant has often been used for a study of crystal imperfections. Unfortunately, in most cases the two types of measurements have been carried out on different specimens or with insufficient accuracy. Therefore the results are not conclusive.

In our study of crystal imperfections, a group of large single crystals was selected. In the foregoing paper<sup>1</sup> were presented the lattice constant measurements; here we report our density determinations.

### MATERIAL

The following single crystals (all cubic except quartz) have been used in our investigation: Si, quartz,  $\text{CaF}_2$ , CsI, Ge, TlCl, TlBr, and, in addition, a polycrystalline sample of Al.<sup>2</sup> Of these, Al is face-centered, CsI, TlCl, and TlBr are body-centered, Si and Ge have the diamond structure and  $\text{CaF}_2$  has a structure similar to diamond. The densities vary considerably from 2.70 to 7.45 g/cm<sup>3</sup>. Also this group of crystals represents the three main bonding types: metallic, ionic, and covalent.

Si crystals<sup>3</sup> were grown in argon and Ge crystals<sup>3</sup> in nitrogen, both from the highest purity materials by the pulling method with a speed of 10 cm/hr.  $\text{CaF}_2$  crystals<sup>4</sup> were grown from selected natural fluorite in a graphite crucible by the Stockbarger method in vacuum, annealed at 800°C for 24 hr and cooled down at a rate of 10°C/hr. CsI was prepared from CsBr, which was converted to  $\text{CsIO}_3$  and this decomposed to CsI. The crystals of CsI were grown by the Bridgman method in sealed Vycor crucibles in an argon atmosphere with a speed of 1 mm/hr. TlCl and TlBr were prepared from pure Tl metal and purified by vacuum distillation. Crystals of TlCl and TlBr were grown in sealed Pyrex crucibles in an argon atmosphere with a speed of 1 mm/hr.

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<sup>1</sup> A. Smakula and J. Kalnajs, *Phys. Rev.* **99**, 1737 (1955), preceding article.

<sup>2</sup> Aluminum has been included because the lattice constant measured by various authors shows the best agreement as compared with other materials.

<sup>3</sup> Material and resistivity data from Raytheon Manufacturing Company, Waltham, Massachusetts (courtesy of Dr. H. Statz).

<sup>4</sup> From Optovac, North Brookfield, Massachusetts.

The strain effect on density was checked on thallium halides, which have the highest expansion coefficients. We were not able to detect any density difference between samples annealed at 380°C for 24 hr and cooled down at a rate of 3°C/hr and unannealed samples. CsI was annealed immediately after growing for 12 hr at 500°C and cooled down at a rate of 15°C/hr. The vacuum-cast Al sample<sup>5</sup> was annealed in an evacuated Pyrex container at 480°C for 24 hr and cooled down at a rate 6°C/hr.

The purity of the crystals was: Al (99.99+%) contained 0.001% Si and a few other elements, each <0.0001%; Si and Ge were characterized by their resistivity of 100 and 40 ohm-cm, respectively; TlCl and TlBr, according to spectroanalysis, showed only traces of a few common elements, a reciprocal contamination by anions was prevented by the use of Br-free HCl and Cl-free HBr<sup>6</sup> for the synthesis; CsI was contaminated by Fe, K, Mg, Na, Sr, and V to <0.001% and by Rb about 0.01%; and  $\text{CaF}_2$  contained <0.001% of Ag, Fe, Mg, and Si, and somewhat more Sr.

### METHOD OF DENSITY DETERMINATION

Since our samples were large (1 to 20 cm<sup>3</sup>), the method of hydrostatic weighing was selected; an Ainsworth's semimicro balance, 100 g maximum load on each pan, rated sensitivity 0.01 mg, was used. The set of weights (Ainsworth, class *M*) was calibrated by the National Bureau of Standards. For volume determination the samples were suspended on a stainless steel wire (2 mils diameter) from the left pan and submerged in the thermostated liquid (Fig. 1). The bath temperature was measured with a thermometer (subdivisions 0.02°C) calibrated by the National Bureau of Standards. The temperature fluctuation in the bath was  $\pm 0.01^\circ\text{C}$  and that of the immersion liquid  $\pm 0.005^\circ\text{C}$ . Because of the water solubility of some crystals, ethylene bromide ( $\text{C}_2\text{H}_4\text{Br}_2$ ) (b.p. 131.6° to 131.8°C at 760 mm Hg) served as immersion liquid. The density of ethylene bromide was determined by a secondary standard, a polished cube of natural quartz crystal. The density of

<sup>5</sup> Material and spectroanalysis from Aluminum Company of America, New Kensington, Pennsylvania.

<sup>6</sup> We wish to thank Malinckrodt Chemical Works for the chlorine-free hydrobromic acid.

the quartz standard is referred to water as the primary standard.

### DENSITY OF WATER

The standard water density is  $d_{25^{\circ}\text{C}} = 0.997048 \text{ g/cm}^3$ , as determined by Chappuis<sup>7</sup> and revised by Tilton and Taylor,<sup>8</sup> if  $1.000027 \pm 2^9$  is used as the conversion factor for milliliter to cubic centimeters. The following factors influence the density of water: (1) The effect of dissolved air is noticeable in the 7th decimal place<sup>10</sup>; (2) the pressure effect is  $\Delta d = +5 \times 10^{-6}$  per atmosphere<sup>11</sup>; for ordinary air-pressure fluctuation of  $\pm 20$  mm Hg,  $\Delta d = \pm 1.3 \times 10^{-6}$ ; (3) the variation in the isotopic composition of natural water influences the density in the 7th place only,<sup>12</sup> provided the purification is done without isotopic fractionation; and (4) the influence of temperature is  $\Delta d = 2.5 \times 10^{-4}$  per  $^{\circ}\text{C}$  at  $25^{\circ}\text{C}$ . A change of temperature of  $0.01^{\circ}\text{C}$  changes the density by  $2.5 \times 10^{-6}$ . Tap water was distilled once and

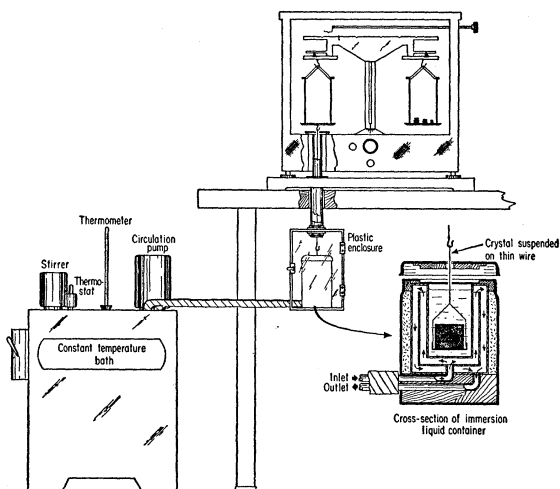


Fig. 1. Apparatus for density determination.

boiled before use; it had a conductivity of  $1.6 \times 10^{-6} \text{ (ohm-cm)}^{-1}$ . According to Kirschenbaum<sup>13</sup> a change of  $1 \times 10^{-6}$  in conductivity causes a change of  $1 \times 10^{-6}$  in density.

### DENSITY OF THE QUARTZ STANDARD

A polished cube (*ca*  $16 \text{ cm}^3$ ) of natural quartz crystal was used. After weighing in air the crystal was placed

<sup>7</sup> P. Chappuis, *Trav. mém. bur. int. poid. mes.* **14**, D1-D63 (DA) (1910).

<sup>8</sup> L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. Standards* **18**, 205 (1937).

<sup>9</sup> R. T. Birge, *Revs. Modern Phys.* **13**, 233 (1941).

<sup>10</sup> N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940).

<sup>11</sup> E. H. Amagat, *Ann. chim. et phys.* [6] **29**, 68, 505 (1893).

<sup>12</sup> E. W. Washburn and E. R. Smith, *J. Research Natl. Bur. Standards* **12**, 305 (1934).

<sup>13</sup> I. Kirschenbaum, *Physical Properties and Analysis of Heavy Water* (McGraw-Hill Book Company, Inc., New York, 1951), p. 295.

TABLE I. Density of natural quartz crystals.

Density as measured	Temperature $^{\circ}\text{C}$	Density computed for $25^{\circ}\text{C}$	Reference
2.650745	0	2.64847	15
$2.64822 \pm 5$	25	$2.64822 \pm 5$	16
2.65074	0	2.64846	17
$2.64875 \pm 8$	18	$2.64810 \pm 9$	18
$2.64845 \pm 1.5$	25	$2.64845 \pm 1.5$	present paper

in a container (Fig. 1) with water and evacuated to remove air bubbles. For a good weighing reproducibility, the suspension wire was cleaned with a solution of potassium hydroxide in methyl alcohol. The height of water was kept at a constant level in all weighings. All weighings were corrected for air buoyancy. The humidity and temperature were measured inside the balance. The crystal density  $d$  has been computed applying all necessary corrections.<sup>14</sup> The mean value of five determinations is given in Table I and, for comparison, published data are listed also.<sup>15-18</sup>

The first value in Table I was obtained on large samples (*ca*  $50 \text{ cm}^3$ ) by comparing the weight with the mass standard (kilogram) and the volume with the length standard (meter). This value is considered the most reliable at present. The other three values are from pycnometric measurements on powdered material. For density computation for  $25^{\circ}\text{C}$  the following expansion coefficients<sup>19</sup> were used:

$$\alpha_{11} = (7.161 + 0.0160 t) \times 10^{-6} / ^{\circ}\text{C};$$

$$\alpha_{12} = (13.255 + 0.0223 t) \times 10^{-6} / ^{\circ}\text{C}.$$

### DENSITY OF Si, Al, $\text{CaF}_2$ , CsI, Ge, TlCl, AND TlBr

The density of the crystals was determined using ethylene bromide as the immersion liquid and quartz as the standard. To exclude any influence of room-temperature fluctuation on the density of ethylene bromide, the quartz standard was weighed before and after the sample weighing and the density of the liquid corrected, if necessary. The reproducibility of our meas-

TABLE II. Density of Si and Ge at  $25^{\circ}\text{C}$ .

Sample	Number of meas.	$d_{25^{\circ}\text{C}} \text{ Si}$	Number of meas.	$d_{25^{\circ}\text{C}} \text{ Ge}$
1	3	$2.32901 \pm 0.00003$	6	$5.32673 \pm 0.00006$
2	3	$2.32900 \pm 0.00004$	4	$5.32674 \pm 0.00001$
3	3	$2.32903 \pm 0.00003$	2	$5.32672 \pm 0.00003$
4	3	$2.32904 \pm 0.00003$		

<sup>14</sup> See, e.g., N. Bauer in *Physical Methods of Organic Chemistry*, edited by A. Weissberger (Interscience Publishers, Inc., New York, 1949), second edition.

<sup>15</sup> I. Mace de Lepinay *et al.*, *Trav. mém. bur. int. poid. mes.* **14**, 120 (1910).

<sup>16</sup> P. H. Miller and J. W. M. DuMond, *Phys. Rev.* **57**, 198 (1940).

<sup>17</sup> T. Batuecas, *Nature* **165**, 62 (1950).

<sup>18</sup> T. Batuecas, *Nature* **173**, 345 (1954).

<sup>19</sup> I. R. Benoit, *Trav. mém. bur. int. poid. mes.* **6**, 1 (1888).

TABLE III. Densities of single crystals in g/cm<sup>3</sup> determined by hydrostatic weighing. Standard: density of water at 25°C=0.997048 g/cm<sup>3</sup>;<sup>a</sup> temperature=25.00±0.01°C.

Crystal	Number of observations <i>k</i>	<i>d</i>	Errors		
			random <sup>b</sup>	systematic <sup>c</sup>	total
Silicon	12	2.32902	1.0×10 <sup>-5</sup>	2.0×10 <sup>-5</sup>	3.0×10 <sup>-5</sup>
Quartz	5	2.64845	1.5	1.0	2.5
Aluminum (polycrystalline)	3	2.69801	1.5	1.5	3.0
CaF <sub>2</sub>	3	3.17934	2.0	3.0	5.0
CsI	3	4.52593	8.0	4.0	12
Ge	4	5.32674	0.5	4.5	5.0
TiCl	3	7.01829	1.0	6.0	7.0
TiBr	3	7.45292	1.0	6.5	7.5

<sup>a</sup> The water density for 25.0°C as given by H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen aus Physik Chemie Astronomie Geophysik und Technik* (Springer-Verlag, Berlin, 1955), Vol. 4, Part 1, p. 102, is  $d_{25} = 0.997046$  g/cm<sup>3</sup>. This small difference could cause a maximum change of  $1.5 \times 10^{-6}$  in densities which is within limits of our accuracy.

<sup>b</sup> Random error =  $[\sum_1^k (d_0 - d)^2 / k(k-1)]^{1/2}$ .

<sup>c</sup> Systematic error =  $(d_{\text{sample}} / d_{\text{quartz}}) \times \text{total error for quartz standard}$ . The systematic error of the density of quartz was computed from the uncertainty of ±0.01°C in the temperature of the water.

urements for four silicon and three germanium samples from different crystals, and the random errors are given in Table II.

The measured densities are shown in Table III with random, systematic and total errors. Comparing the data for Si and Ge from Tables II and III, one finds that the difference between the various samples varies no more than the random error.

In Table IV are given the published densities of the crystals.<sup>16,20-25</sup> Only in the case of quartz is there an agreement between the older and our present values. All other values differ considerably. The difference may be caused by density variation of samples, influence of adsorbed air in powder measurements or temperature deviation.

### CONCLUSIONS

Our measurements show that the density of large single crystals can be determined by hydrostatic weighing with an accuracy of 0.001 to 0.002 percent. Various specimens of silicon and germanium show

<sup>20</sup> M. E. Straumanis and E. Z. Aka, *J. Appl. Phys.* **23**, 330 (1952).

<sup>21</sup> J. L. Snoek, *Phil. Mag.* **41**, 1188 (1950).

<sup>22</sup> H. E. Mervin, *Am. J. Sci.* [4] **32**, 429 (1911).

<sup>23</sup> G. P. Baxter and C. C. Wallace, *J. Am. Chem. Soc.* **38**, 264 (1916).

<sup>24</sup> E. Cohen and K. Piepenbroek, *Z. physik. Chem.* **A167**, 388 (1933).

<sup>25</sup> F. W. Clarke and H. Keck, *J. Am. Chem. Soc.* **5**, 241 (1884).

TABLE IV. Published densities.

Subst.	Density	Temperature °C	Lin. exp. coeff. ×10 <sup>6</sup>	Computed dens. 25°C	Reference
Si	2.32831±31	20	4.15	2.3282±3	20
Al	2.69892	20	23.29	2.69798	21
Al	2.69839±38	25	...	2.69839±38	16
CaF <sub>2</sub>	3.180	20	19	3.179	22
CsI	4.509	25	48.6	4.509	23
Ge	5.3234±25	25	5.92	5.3234±25	20
TiCl	7.0000±4	30	54.6	7.0057±4	24
TiBr	7.540	21.7	51.2	7.537	25

constant density within the limit of our measurements. However, there is a disagreement between the older and our values. The difference may be caused by the material or experimental errors. Our result for the density of quartz agrees well with older measurements but not with a newer value of Batuecas. In all density measurements one has to remember that absolute density values depend on water density as primary standard, which is in error by at least  $2 \times 10^{-6}$ . It will be seen from the accompanying paper<sup>26</sup> that our weighing densities are in good agreement with densities computed from the lattice constants obtained from the same samples.

<sup>26</sup> Smakula, Kalnajs, and Sils, *Phys. Rev.* **99**, 1747 (1955), following article.