PHYSICAL REVIEW VOLUME 99, NUMBER 6 SEPTEMBER 15, 1955

Densities and Imperfections of Single Crystals*

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(Received June 3, 1955)

The densities of Si, Al, CaF_2, CsI, Ge, TlCl, TlBr, and SiO_2 (quartz) have been computed from lattice constants and molecular weights obtained from International Atomic Weights, and compared with the densities as determined by hydrostatic weighing of large single crystals. The hydrostatic density of Ge proves too large by 0.00193. This discrepancy disappears when the mass-spectroscopic atomic weight is used for the density calculation. Also for Si, Al, and CaF_2 a better agreement results with mass-spectroscopic atomic weights. Therefore, we conclude that the mass-spectroscopic atomic weights are more reliable than the officially accepted ones. From measured densities and lattice constants of Si, Al, CaF_2, and Ge, Avogadro's number is obtained as 6.02368×10^{23} mole^{-1} (chemical scale). The relative density defects for our samples of Si, Al, CaF_2, and Ge proves to be negligible within the limit of our measurements ($<5\times10^{-6}$). We consider these crystals the most perfect that we have obtained up to the present time. A somewhat higher relative density defect in quartz (11×10^{-6}) may be caused by uncertainty of the data used for the computation of the density and that for CsI (13×10^{-6}) by Rb contamination. TlCl and TlBr show the greatest relative density defects, 43×10^{-6} and 40×10^{-6}, respectively. These crystals may contain vacancies or dislocations in the order of $\sim5\times10^{18}$ per cc, as is known also for the silver halides.

INTRODUCTION

Natural and synthetic crystals contain imperfections in the form of impurities and crystal defects (lattice vacancies, dislocations, etc.). Since most of the physical properties are influenced by such imperfections to some extent, their study is one of the important problems of solid-state research.

One of the most direct methods of detecting crystal imperfections is the precision determination of densities. This can be done by determining mass and volume with a balance, or by calculating the mass from the molecular weight and Avogadro's number, using the lattice constant for the volume determination. While the first method gives an average of the density taken over a large volume, the second method gives the ideal density of the crystal lattice. The two densities can be equal only in ideal crystals. In real crystals a difference is to be expected, which gives information about the crystal imperfections. If the macroscopic density is higher than the microscopic, interstitials are present; if it is lower, vacancies (Schottky defects) or one or another kind of dislocations predominate. In case of impurities their effect on density can be positive or negative, depending on the ionic radius, atomic weight and how they are built into the lattice (interstitially or substitutionally). Instead of referring to densities, one can compare atomic weights with those obtained by chemical or mass-spectroscopic methods or compare Avogadro's number with a standard value.

Such investigations have been made in recent years by various authors.[1–5] The published results, however, differ considerably or are even contradictory. For instance, according to Straumanis[2] Al and Si[3] should have interstitials, but according to Addink[4] both should have vacancies. For Avogadro's number (chemical scale) Birge's[5] value is 6.02338×10^{23} mole^{-1}, Straumanis[2] uses 6.02403×10^{23} mole^{-1} and Addink's best value is 6.0228×10^{23} mole^{-1}. This study was therefore undertaken with the aim of deciding whether or not, at the present time, valid conclusions can be drawn on crystal imperfections from density determinations.

Our investigation differs from older ones in the following points:

(1) We used a group of crystals differing in lattice constants, densities and chemical bonding.

(2) The lattice constants and densities were measured on the same samples and at the same temperature.

Table I. Physical constants of crystals used for density computation.

	Crystal	n	$a_{25°C}$ [a]	Ref. lattice constant	Atomic or molecular weight Internat.	Mass-spec.[b]	Ref. mass-spec.
1	Si	8	5.43072 A	6	28.09	28.0875	10
2	Al	4	4.04960	6	26.98	26.98256	11
3	CaF_2	4	5.46342	6	78.08	78.079	12
4	CsI	1	4.56772	6	259.82	259.821	13, 14
5	Ge	8	5.65753	6	72.60	72.630	15
6	TlCl	1	3.84247	6	239.847	239.852	16
7	TlBr	1	3.98588	6	284.306	284.301	16
8	SiO_2	3	a: 4.91329	9	60.09	60.0875	10, 17
			c: 5.40483	9			

[a] For $CuK\alpha_1$ ($\lambda=1.54051$ A).
[b] Chemical scale.

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* Sponsored by the Office of Naval Research, the U. S. Army Signal Corps, the U. S. Air Force, and the U. S. Ordnance Materials Research Office.

[1] Y. Tu, Phys. Rev. **40**, 662 (1932); D. A. Hutchison and H. L. Johnston, J. Am. Chem. Soc. **62**, 3165 (1940); Phys. Rev. **62**, 32 (1942); P. M. Miller and J. W. DuMond, Phys. Rev. **57**, 198 (1940); D. A. Hutchison, Phys. Rev. **66**, 144 (1944); J. Chem. Phys. **13**, 383 (1945); M. E. Straumanis, Z. Physik **126**, 49 (1949); Am. Mineralogist **38**, 662 (1953); Phys. Rev. **95**, 566 (1954); T. Batuecas, Nature **165**, 61 (1940); **173**, 345 (1954).

[2] M. E. Straumanis, Acta Cryst. **2**, 82 (1949).

[3] M. E. Straumanis and E. Z. Aka, J. Appl. Phys. **23**, 330 (1952).

[4] N. W. H. Addink, Rec. trav. chim. **70**, 202 (1951).

[5] R. T. Birge, Am. J. Phys. **13**, 63 (1945).

TABLE II. Avogadro's number as given in the literature from 1945 to 1954.

Reference	$N_0 \times 10^{-23}$ mole^{-1} Physical scale	Chemical scale	Conversion factor phys. to chem. scale
1. Birge[a] 1945	6.02506±23	6.02338±23	1.000279[b]
2. DuMond and Cohen[c] 1948	6.0251±4	6.0235±4	1.000266[b]
3. Straumanis[d] 1949	6.02567±30	6.02403±30	1.000272[b]
4. Kirchner[e] 1950	6.0252±15	6.0236±15	1.000266[b]
5. DuMond and Cohen[f] 1950	6.025438±107	6.023762±107	1.0002783[17]
6. Bearden and Watts[g] 1951	6.02566±16	6.02402±17	1.000272[b]
7. Witmer[h] 1951	6.02601±35	6.02433±35	1.0002783[17]
8. Stille[i] 1952	6.02533±15	6.02365±15	1.000279[b]
9. DuMond and Cohen[j] 1952	6.02544	6.02376	1.0002783[17]
10. DuMond and Cohen[k] 1954	6.02472±36	6.02304±36	1.0002783[17]
11. Brogren (quartz)[l] 1954	6.02540	6.02372	1.0002783[17]
12. Brogren (calcite)[l] 1954	6.02495	6.02327	1.0002783[17]

[a] See reference 5.
[b] Obtained as ratio of physical to chemical scale.
[c] See reference 22.
[d] See reference 2.
[e] See reference 23.
[f] See reference 24.
[g] See reference 25.
[h] See reference 26.
[i] See reference 27.
[j] See reference 20.
[k] See reference 21.
[l] See reference 9.

(3) We used molecular weights computed from masses and abundances of atomic isotopes.

MATERIAL

Large single crystals of Si, Ge, CaF_2, TlCl, TlBr, CsI, and SiO_2 (natural quartz) and polycrystalline Al of very good quality were selected. Most of them belong to the cubic system; Si and Ge have diamond structure, CaF_2 is diamond-like; TlCl, TlBr and CsI have a body-centered structure; Al is face-centered cubic and SiO_2 (quartz) hexagonal. These crystals represent the three types of bonding: covalent, ionic, and metallic. In consequence, we expect various types of imperfections, expressing themselves in a different influence on lattice constant and density. The Al sample (vacuum-cast) was polycrystalline, but is included here because the published lattice constants for Al show the best agreement of all measured materials.[6] The purity of the crystals is given in the preceding paper.[7]

X-RAY DENSITIES AND COMPARISON WITH DENSITIES OBTAINED BY WEIGHING

The densities were computed for cubic crystals as $d_x = nA/a^3N$ (for quartz $d_x = 2nA/3a^2cN$), where n is the number of molecules per unit cell, A the atomic or molecular weight, a the lattice constant, and N Avogadro's number. The value for n, A, and a are listed in Table I. The atomic weights are those recommended by the International Commission on Atomic Weights,[8] and the lattice constants are those of the accompanying paper[6] and of Brogren.[9] In addition, in Table I atomic and molecular weights[10–17] computed from masses and abundances of atomic isotopes are given for later use.

The absolute error of the lattice constant is higher than the random error (±0.00002 A) because of the uncertainty of the x-ray wavelength by ±0.00006 A.[18] Cu $K\alpha_1$ ($\lambda = 1.54051$ A) was used, as recommended by Lonsdale.[19] For Avogadro's number the published data vary considerably. Table II contains the data published during the past ten years.[2,5,9,20–27] Some of these

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[6] A. Smakula and J. Kalnajs, this issue [Phys. Rev. **99**, 1737 (1955)].

[7] A. Smakula and V. Sils, this issue [Phys. Rev. **99**, 1744 (1955)].

[8] E. Wichers, J. Am. Chem. Soc. **76**, 2033 (1954).

[9] Computed for 25°C from data given for 18°C by G. Brogren, Arkiv Fysik **7**, 47 (1954), using linear expansion coefficients

$$\alpha_{\parallel} = (7.161 + 0.0160\, t) \times 10^{-6}/°\text{C}$$

and

$$\alpha_{\perp} = (13.255 + 0.0223\, t) \times 10^{-6}/°\text{C}$$

taken from I. R. Benoit, Trav. mém. bur. int. poid. mes. **6**, 1 (1888).

[10] Masses from: Duckworth, Preston, and Woodcock, Phys. Rev. **79**, 188, 402 (1950). Abundances from: (*a*) M. G. Inghram, Phys. Rev. **70**, 653 (1946); (*b*) E. P. Ney and J. H. McQueen, Phys. Rev. **69**, 41 (1946); (*c*) D. Williams and P. Yuster, Phys. Rev. **69**, 556 (1946); (*d*) J. R. White and A. E. Cameron, Phys. Rev. **74**, 991 (1948); (*e*) R. F. Hibbs as reported by K. T. Bainbridge and A. O. Nier, Preliminary Report No. 9, Nuclear Science Series (National Research Council, Washington, 1950); (*f*) J. H. Reynolds, Phys. Rev. **90**, 1047 (1953); average taken from (*a*) to (*f*)

[11] C. W. Li, Phys. Rev. **88**, 1038 (1952).

[12] Masses for calcium from: Collins, Nier, and Johnson, Jr., Phys. Rev. **84**, 717 (1951). Abundances for calcium from: J. R. White and A. E. Cameron, Phys. Rev. **74**, 991 (1948).

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[14] R. E. Halsted, Phys. Rev. **88**, 666 (1952), I.

[15] Masses from: Collins, Johnson, and Nier, Phys. Rev. **94**, 398 (1954). Abundances from: (*a*) R. F. Hibbs as reported by K. T. Bainbridge and A. O. Nier, Preliminary Report No. 9, Nuclear Science Series (National Research Council, Washington, 1950); (*b*) Inghram, Hayden, and Hess, Report, Argonne National Laboratory Report, ANL-4082, 1947 (unpublished, p. 5); average taken of both. Because of large errors the recent data of J. H. Reynolds, Phys. Rev. **90**, 1047 (1953) have not been used.

[16] T. L. Collins (private communication).

[17] A. O. Nier, Phys. Rev. **77**, 789 (1950).

[18] W. L. Bragg, J. Sci. Instr. **24**, 27 (1947).

[19] K. Lonsdale, Acta Cryst. **3**, 400 (1950).

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[22] J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. **20**, 82 (1948).

[23] F. Kirchner, *Landolt-Börnstein Tabellen* (Springer-Verlag, Berlin, 1950), sixth edition, Vol. I, Part 1.

[24] J. W. M. DuMond and E. R. Cohen, Phys. Rev. **82**, 555 (1951).

[25] J. A. Bearden and H. M. Watts, Phys. Rev. **81**, 73 (1951).

[26] E. E. Witmer, Phys. Rev. **81**, 308 (1951).

[27] U. Stille, Physik. Bl. **9**, 397 (1952).

values were computed from densities and lattice constants obtained on different samples: others were derived from different physical constants. We decided to use Birge's value since it is based on the same kind of measurements as ours, and served as a starting value for the computation of the universal physical constants.[20,21]

Our densities are given (Table III) under d_{x1} computed using International Atomic Weights and under d_w those determined by hydrostatic weighing.[7]

(a) Influence of Atomic Weight on Density

In Fig. 1, Δd_{x1} is plotted *vs* d_w. For most crystals the difference Δd_{x1} proves to be smaller than 0.0008, except for Ge. Initially we assumed that the large deviation for Ge was caused by interstitials.[28] However, doubt arose when no comparable deviation was found for Si. The only other possibility for the great deviation in Ge was a corresponding error in the atomic weight.The value of the atomic weight given to Si has been changed in recent years[29] by three units in the second decimal place because of new determinations by chemical and mass-spectroscopic methods. The last atomic weight determination of Ge was made by a chemical method.[30] No mass-spectroscopic atomic weight of Ge has been published. Through the courtesy of Professor K. T. Bainbridge and Dr. T. L. Collins, Harvard University, the atomic weight for Ge was obtained as calculated from mass-spectroscopic data. This value, together with those for the other crystals, is listed in Table I. With these mass-spectroscopic molecular weights, the densities for our crystals assume the value d_{x2} (Table III). Δd_{x2} gives the density difference between these computed (d_{x2}) and the measured values d_w. As seen from Table III and Fig. 1, the great density difference in Ge disappears and the differences for most of the other crystals are much reduced. A slight increase occurs for TlCl. We can conclude that the density differences for most of our crystals were caused by the uncertainty of the atomic weights.

TABLE III. Comparison of densities determined by weighing (d_w), and computed from lattice constants (Table I), using molecular weights from international atomic weights (d_{x1}) and from masses and abundances of isotopes (d_{x2}), the Avogadro number of Birge (6.022338×10^{23} mole^{-1}), and temperature 25.0°C. $\Delta d_{x1}=d_{x1}-d_w$, $\Delta d_{x2}=d_{x2}-d_w$.

	d_w	d_{x1}	Δd_{x1}	d_{x2}	Δd_{x2}	$\Delta d_{x2}:d_w$
Si	2.32902	2.32932	0.00030	2.32912	0.00010	0.000043
Al	2.69801	2.69790	−0.00011	2.69815	0.00014	0.000052
CaF_2	3.17934	3.17955	0.00021	2.17951	0.00017	0.000053
CsI	4.52593	4.52620	0.00027	4.52622	0.00029	0.000064
Ge	5.32673	5.32480	−0.00193	5.32700	0.00027	0.000051
TlCl	7.01829	7.01880	0.00051	7.01894	0.00065	0.000093
TlBr	7.45292	7.45372	0.00080	7.45359	0.00067	0.000090
Quartz	2.64845	2.64866	0.00021	2.64855	0.00010	0.000038

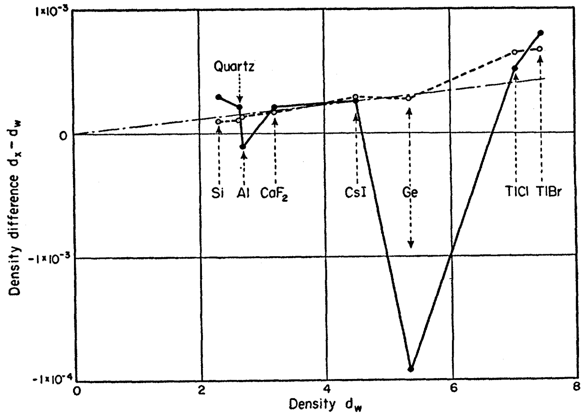

FIG. 1. Difference of x-ray and weighing density $d_x-d_w=\Delta d_x$. For computing x-ray density: Cu $K\alpha_1$ $\lambda=1.54051$ A and Birge's Avogadro number 6.02338×10^{23} mole^{-1}. Solid circles, Δd_{x1}, international atomic weights used; open circles, Δd_{x2}, mass-spectroscopic atomic weights used.

(b) Influence of Lattice Constant on Density

The random error of our lattice constants for all crystals is ±0.00002 A.[6] The systematic error caused by the uncertainty of the x-ray wavelength is 0.004 percent. Since we used the same wavelength (Cu $K\alpha_1$) in all our lattice-constant determinations, this error is a constant factor for all of the crystals. The lattice constants are influenced proportionally to their absolute values. The influence of the lattice-constant error on density can not be separated from the error of Avogadro's number.

(c) Influence of Avogadro's Number on Density

While A and a vary from crystal to crystal, N is a constant, therefore its influence on $\Delta d_{x2}:d_w$ must be a constant. In Fig. 2, $\Delta d_{x3}:d_w$ is plotted *vs* d_w. All values are positive and very nearly equal. This could be interpreted by vacancies. However, this interpretation would lead to the improbable consequence that all of our crystals (except TlCl and TlBr) have an equal number of vacancies. We therefore assume that our product a^3N is not correct. The absolute error of a and N is practically the same (~0.0002). Since a is based on the crystallographic conversion factor $\lambda_{\mathrm{abs}}:\lambda_{kx}$ which is at present generally accepted, we keep a constant

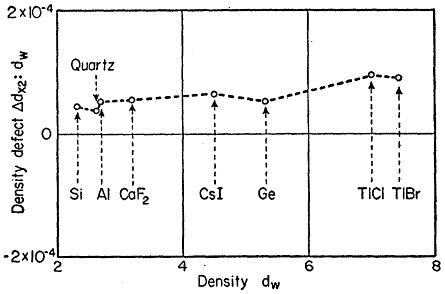

FIG. 2. Relative density defects ($\Delta d_{x2}:d_w$). (We used $N=6.02338\times10^{23}$ mole^{-1} and mass-spectroscopic atomic weights.)

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[28] Smakula, Kalnajs, and Sils, Phys. Rev. **97**, 253 (1955).

[29] E. Wichers, J. Am. Chem. Soc. **74**, 2446 (1952).

[30] Hönigschmid, Wintersberger, and Wittner, Z. anorg. u. allgem. Chem. **225**, 81 (1935).

TABLE IV. Avogadro's number N (chemical scale) computed from densities, lattice constants (Cu $K\alpha_1\lambda = 1.54051$ A) mass-spectroscopic atomic weights (conversion factor from physical to chemical scale 1.0002783[17]).

Crystal	N (mole^{-1})
Si	6.02364×10^{23}
Al	6.02370×10^{23}
CaF$_2$	6.02370×10^{23}
Ge	6.02369×10^{23}
Mean value:	6.02368×10^{23}

TABLE V. Comparison of densities determined by weighing (d_w), and computed (d_{x3}) from lattice constants using mass-spectroscopic atomic weights and $N = 6.02368\times10^{23}$ mole^{-1} for temperature 25.0°C.

	d_w	d_{x3}	Δd_{x3}	$\Delta d_{x3}:d_w$
Si	2.32902	2.32901	−0.00001	−0.0000043
Al	2.69801	2.69802	0.00001	0.0000037
CaF$_2$	3.17934	3.17935	0.00001	0.0000031
CsI	4.52593	4.52599	0.00006	0.000013
Ge	5.32673	5.32674	0.00001	0.0000019
TlCl	7.01829	7.01859	0.00030	0.000043
TlBr	7.45292	7.45322	0.00030	0.000040
Quartz	2.64845	2.64842	−0.00003	−0.000011

and correct N. N-values computed from four of our best crystals (Si, Al, CaF$_2$, and Ge) are given in Table IV. The mean value is $(6.02368\pm0.00002)\times10^{23}$ mole^{-1}.

Using this Avogadro's number, and atomic and molecular weights computed from mass-spectroscopic data and our lattice constants, the final densities d_{x3}, differences $\Delta d_{x3} = d_{x3} - d_w$ and $\Delta d_{x3}:d_w$ = relative density defects are computed (Table V and Fig. 3).

CONCLUSIONS

A study of crystal imperfections by density measurements requires a knowledge of atomic weights, lattice constants, and Avogadro's number to a high accuracy. We found that the international atomic weights are sometimes unreliable and have to be replaced by more accurate data obtained from masses and abundances of atomic isotopes. The values of lattice constants are based on the absolute values of the x-ray wavelengths; these are obtained from Siegbahn kX units by multiplication with a conversion factor $f = \lambda_g/\lambda_s$. We can use either the crystallographic conversion factor 1.002026, or the Universal 1.002063 (computed by DuMond and Cohen[21]). In the former case Avogadro's number in the chemical scale is 6.02368×10^{23} mole^{-1} and in the latter 6.02301×10^{23} mole^{-1}, which is very close to DuMond and Cohen's value 6.02304×10^{23} (see Table II). Only two of the previous N values, those from KCl[5] and from quartz, are close to ours; the value obtained from calcite by Brogren[9] is lower and that by Straumanis[2] is higher. The discrepancy for calcite is probably caused by impurities.[31,32] Calcite can hardly qualify as a standard crystal. Even if its impurities are determined, a correction for molecular weight cannot be made as long as it is not known whether impurities are bound substitutionally or interstitially.

Of the crystals studied here, Si, Al, CaF$_2$, and Ge contain relative density defects, $\Delta d_{x2}:d_w$, which are less than 5×10^{-6}, that is, undetectable within the limit of our measurements. The values 11×10^{6} for quartz and 13×10^{-6} for CsI are still close to this limit. The only cases where we have an indication of imperfections are TlCl and TlBr. In both crystals the relative density defects are *ca* 4×10^{-5}. Relative density defects of 22×10^{-5} and 8×10^{-5} have been found recently in AgCl and AgBr single crystals.[33] Since silver and thallium halides are similar in various properties (broad ultraviolet absorption bands, high plasticity, low melting points, etc.), they may have the same kind of imperfections.

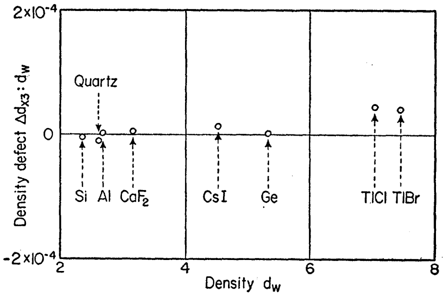

FIG. 3. Relative density defects ($\Delta d_{x3}:d_w$). (We used $N = 6.02368\times10^{23}$ mole^{-1} and mass-spectroscopic atomic weights.)

ACKNOWLEDGMENTS

We are greatly indebted to Professor A. R. von Hippel for his interest and advice in this work.

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