[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE COMPRESSIBILITY OF TELLURIUM

BY ROBERT FRANKLIN MEHL[1] AND BEVERIDGE JAMES MAIR

RECEIVED MARCH 28, 1927 PUBLISHED AUGUST 5, 1927

Although the cubic compressibilities of a large number of elements have been determined in the Harvard Chemical Laboratories during the last twenty-five years by Richards and his collaborators,[2] thus far tellurium has escaped attention.

Four years ago P. W. Bridgman, in the Jefferson Physical Laboratory, determined the linear compressibility of a single crystal of tellurium[3] and discovered the surprising fact that an increase in hydrostatic pressure caused an increase in length along the axis under observation. In a later paper[4] Bridgman redetermined this coefficient on a casting in which the axis measured corresponded closely to the trigonal axis, and also determined the linear compressibility coefficient perpendicular to this axis. These two values for initial linear compressibility at 30° are, respectively, -0.4137×10^{-6} and $+2.748 \times 10^{-6}$, leading to a positive value for the initial cubic compressibility at 30° of 5.082×10^{-6}, pressures always given in kg./cm.^{2}. Bridgman pointed out in this second paper that the value found for the initial cubic compressibility does not fall on the periodic compressibility curve of Richards[5] when atomic weights are used, but does fall on a smooth curve through the values for the neighboring elements when atomic numbers are used.

In order to study further the remarkable behavior of this element it was thought advisable to make a direct determination of the cubic compressibility.[6] A negative coefficient of cubic compressibility is of course contrary to ordinary ideas of pressure and its effects and indeed to the principle of Le Chatelier, but the case of a negative coefficient of linear compressibility is somewhat less clear. It will be shown that this negative coefficient is completely orthodox. The compressibility of tellurium, however, is interesting from another point of view. With iodine it constitutes one of the three pairs of elements showing a reversed order in the periodic table from that of the atomic weights. These exceptional

---

[1] National Research Fellow.

[2] The results of most of these determinations have been given in a summary paper by T. W. Richards, THIS JOURNAL, **37**, 1643 (1915).

[3] Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 5 (1923).

[4] Bridgman, *ibid.*, **60**, 370 (1925).

[5] Richards and others, *Carnegie Inst. Wash. Pub.*, **76**, 66 (1907).

[6] Bridgman's second paper came to the authors' attention after the work reported here had been completed, and while there is overlapping to a small extent the point of view of the present paper is thought to be sufficiently distinct to merit a separate statement.

elements should serve to emphasize the dependence of compressibility upon the extra-nuclear electronic structure of the atom, that is, the compressibility values of the elements in these pairs should fall on a smoothly sloping curve through the values of the neighboring elements when plotted according to atomic numbers but not when plotted according to atomic weights. One of the remaining pairs, argon and potassium, is useless for the purpose since argon is a gas, and the other, nickel and cobalt, is of little use because the compressibilities of these two elements are nearly identical,[7] falling upon a flat portion of the periodic curve of Richards. Tellurium, however, should fall upon a steeply rising portion of the curve, since tin and antimony on its left have coefficients of 1.9×10^{-6} and 2.4×10^{-6}, respectively, and iodine and cesium on its right (when atomic numbers are used) have coefficients of 13.0×10^{-6} and 61×10^{-6} (xenon, a gas, is of course omitted).[8]

Method

The methods used to determine the compressibility coefficient of tellurium and to standardize the piezometer with which the measurements were made have been described elsewhere in considerable detail[9] and will not be given here. The measurements were made at 25° instead of the usual 20°, however, and it was necessary to determine a new correction factor for water to apply at this higher temperature.[10] This factor could, of course, be calculated[11] but it was thought better to determine it directly, especially since a direct determination would provide a dependable value for the compressibility of water at 25°, a datum not hitherto available.[12]

The greatest difference between the amounts of water used in the de-

---

[7] Bridgman, *Proc. Am. Acad. Arts Sci.*, **58,** 5 (1923), found the compressibility coefficient of nickel to be 0.529×10^{-6} and that of cobalt 0.539×10^{-6}, both at 30°.

[8] Richards, This Journal, **37,** 1643 (1915).

[9] Richards, *J. Franklin Inst.*, **198,** 25 (1924); also Richards and Saerens, This Journal, **46,** 935 (1924).

[10] Richards and Sameshima, This Journal, **42,** 49 (1920), used 0.2069 as the factor to be applied at 25°. This factor presumably was calculated from approximated values for the compressibility of water and that of mercury at 25°. The approximate nature of the factor used has no bearing upon the accuracy of the results obtained, since the amount of water used in each determination was nearly equal to that used in the standardization, so that the inaccuracy in the correction factor, appearing in the third decimal place, does not appear in the compressibility coefficients calculated. The compressibility coefficient for mercury at 25° used in the present work, namely, 4.00×10^{-6}, was taken from this previous paper.

[11] Richards, *Carnegie Inst. Wash. Pub.*, **76,** 33, 36 (1907).

[12] Amagat, *Ann. chim. phys.*, [6] **29,** 68, 505 (1893), determined the compressibility of water at 20° and 30° in intervals of 100 atm. between 100 and 500 atm. (and beyond). From these data an approximate value may be obtained for the average compressibility between 100 and 500 megabars and at 25°, namely, 41.9×10^{-6}. The value here determined directly is lower, and accurate to an additional decimal place.

terminations upon tellurium and that used in the standardization of the piezometer was 2.9993 g. A quantity of water roughly ten times as great was used for the determination of the water correction factor, in order to obtain a value sufficiently exact for the purpose without making a large number of determinations. Two experiments were carried out, yielding four values. These are given in Table I, together with the standardization factors of the piezometer used.

TABLE I

STANDARDIZATION OF PIEZOMETER

Wt. of water, 2.7928 g.
Wt. of mercury, 100–500 megabars.

0.7973 .7966	0.8003 .7931
.7981 .7985	.7942 .7908
.7938 .8008	Average 0.7964 g.[a]

DETERMINATION OF WATER FACTOR

	Expt. No. 1	Expt. No. 2
Total wt. of water taken	26.8316 g.	27.1450 g.
Total wts. of mercury, 100–500 megabars	5.712 5.720 g.	5.764 5.780 g.
Wt. of mercury, 100–500 megabars, in excess of that used in standardization	4.916 4.924 g.	4.968 4.984 g.
Wt. of water in excess of that used in standardization	24.0388 g.	24.3522 g.
Water factor: wt. of mercury, 100–500 megabars per 1 g. of water	$\frac{4.916}{24.039} = 0.2045$ $\frac{4.924}{24.039} = 0.2048$	$\frac{4.918}{24.352} = 0.2040$ $\frac{4.984}{24.352} = 0.2044$
	Average:	0.2044

[a] These values refer to a common quantity of water, namely, 2.7928 g., and have been found by converting the original values to this basis by applying the water correction factor for the difference. The bracketed values represent the pairs obtained from single standardizations.

The compressibility of water may be calculated from the above data in the usual way, after correction is made for the air displaced by the weight of water in excess of that used in the standardization.[13] The four determinations yield values for $\beta_{H_2O,\,25°}$ of 41.55×10^{-6}, 41.60×10^{-6}, 41.45×10^{-6}, and 41.57×10^{-6}, with an average value of 41.54×10^{-6}.

---

[13] The water correction factor is applied to differences of water as weighed in air and no correction for air displacement during weighing is necessary, but, since compressibility refers to true volume, appropriate correction for the air displaced by the water and the weights must be made.

Materials

Tellurium: An analysis showed 99.98% of tellurium;[14] no attempt was made to determine the nature of the impurity present since it is known that impurities in such quantities have a negligible effect upon compressibility with the order of accuracy now attainable.

In order to eliminate voids as much as possible the tellurium was remelted in a Pyrex tube and cast in such a way as to form a single crystal.[15] The tube was chosen of such a size that the casting obtained fitted closely to the piezometer barrel, in order that the quantity of water might be kept at a minimum. The castings obtained, length 22.0 cm. and diameter 1.5 cm., were beautifully crystalline, showing a series of parallel plane markings along which the crystal tended to crack, inclined steeply to the longitudinal axis.

The density was determined upon fragments of the crystal after the compressibility determinations had been made. The usual water displacement method was used with especial care to have possible fissures filled with water. This was done by first immersing the fragments in a large tube nearly filled with water and evacuating the free space. Under this treatment the air held by the crystal greatly expanded, and it became an easy matter to remove the bubbles formed. The crystals were then promptly transferred to a vessel of water in which they were to be weighed. Three determinations upon different pieces gave values for the density of tellurium of 6.258, 6.262, 6.262, average, 6.261, correction having been made for displacement of air.[16]

Determination of Compressibility

The compressibility data are given in Table II.

TABLE II

COMPRESSIBILITY DATA

Wt. of unicrystalline casting: 133.514 g.

Piezometer constant: 0.7964 g. mercury with 2.7928 g. water.

Amt. of water used	Mercury, 100–500 megabars	$\beta \times 10^6$	Av. values
5.5652	1.4796	5.01	5.01
	1.4796	5.01	
5.7707	1.5210	5.00	5.01
	1.5234	5.02	
5.7921	1.5189	4.95	5.00
	1.5300	5.04	
5.8692	1.3363	5.00	5.00
	1.3363	5.00	
3.9670	1.1486	4.89	4.97
	1.1667	5.04	
4.2473	1.2222	5.02	5.02
	1.2213	5.02	

---

[14] This material was very kindly furnished by Mr. Willis T. Burns, manager of the Raritan Copper Works, Perth Amboy, New Jersey. It had been refined from a cruder sample containing 1% of selenium.

[15] The technique used by Bridgman, Ref. 3, was used here without modification.

[16] Kahlbaum, *Z. anorg. Chem.*, **29,** 289 (1902), found 6.235, and Beljankin, *J. Russ. Phys. Chem. Soc.*, **33,** 670 (1901), found 6.338.

The figures here given have their usual significance. Each experiment yielded two (bracketed) figures, the first representing the descent from 500 to 100 megabars and the second the ascent from 100 to 500 megabars made without refilling. It was thought better to start at the higher pressure in order to set the stopper more firmly and quickly, for any progressive settling would cause a lack of coincidence between the two legs of the pressure-volume curve. The correspondence between the members of each pair of figures illustrates the reproducibility of the method, but comparison between separate determinations should be made with the average value for each pair. This is done in the last column of the table, and the agreement between the average values may be seen to be very close.

After a number of determinations had been made the tellurium was remelted and recast, and additional determinations were made in order to free the measurements from any suspicion of error occasioned by imperfections in the original casting. These are the last two determinations in Table II, and they agree with the preceding values within the limit of accuracy, though the first is probably somewhat low.

The average of these six determinations, 5.00×10^{-6}, which represents the average compressibility between 100 and 500 megabars, is probably accurate to within two in the second decimal place.[17]

Discussion

Fig. 1 shows that the value here determined for the compressibility of tellurium fits nicely upon a smooth curve through the corresponding values for tin, antimony, iodine and cesium when the elements are plotted along the abscissa according to atomic numbers, and that the order of the compressibility coefficients is the same as that of the atomic volumes.[18]

---

[17] The value calculated by Bridgman from the linear compressibilities parallel to the trigonal axis and perpendicular to it, 5.082×10^{-6}, represents the initial compressibility at 30°, pressure taken in kg./cm.^{2}. This can be transformed to a value representing the average compressibility between 100 and 500 megabars at 25° by correcting for the difference in temperature, the difference in pressure units and the difference in pressure range. The first two corrections will tend to increase Bridgman's value, since the compressibility has been found to increase with falling temperature, and since the volume change per megabar is greater than per kg./cm.^{2}, but the third correction tends to decrease it, since the compressibility here decreases with increasing pressure. The corrected value is 5.12×10^{-6}, and is appreciably higher than the value determined here. Bridgman does not state how closely the axis measured corresponded to the true trigonal axis; a small variation would be sufficient to account for the discrepancy, since the coefficients for the two axes are so greatly different.

It would appear, therefore, that Richards' method is simpler for the determination of volume compressibility, since no attention need be paid to crystallographic orientation, though for this reason it furnishes no information whatever concerning compressibility anisotropy.

[18] The atomic volumes have been calculated from the density data given in the International Critical Tables, Vol. I, page 103.

It is evident, therefore, that the mass of the nucleus has, so far as these measurements can show, a negligible effect upon compressibility. With the interpretation of the other periodic properties upon the basis of the extra-nuclear atom following the work of Moseley, compressibility, shown by Richards to be a periodic function, likewise received the common explanation. The significance of the present work, therefore, is chiefly one of emphasis and confirmation.

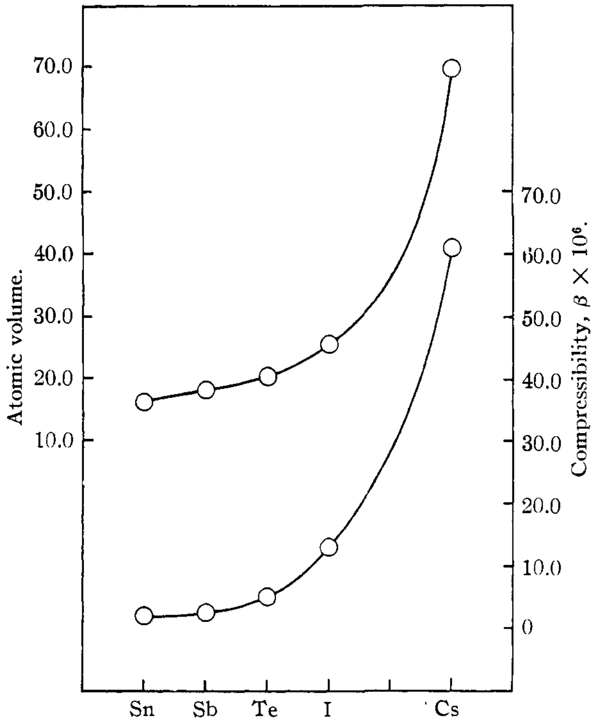

Fig. 1.

Analysis of the curve given in Fig. 1 is beyond hope at present, and will probably not be made until the positions of the electronic orbits in each element and the interaction of the electrons, and also the directive interatomic forces, related to the crystal structure, are understood.

There now remains only to explain the remarkable negative coefficient of linear compressibility found by Bridgman. This effect was observed for tellurium alone, and Bridgman attempted no explanation.

The crystal structure of tellurium is well known.[19] The atoms are arranged on a triangular lattice, the side of the unit basal triangle, *a*, measuring 4.445 Å., and the height of the unit prism, *h*, 5.912 Å. The

---

[19] Slattery, *Phys. Rev.*, [2] **21**, 378 (1923). Bradley, *Phil. Mag.*, **48**, 477 (1924).

density of the element requires three tellurium atoms associated with each lattice point. These atoms are arranged around the prism edge to form an ascending helix, with a threefold symmetry, each atom exactly above the third atom below in the same helix; the prism edge is thus a screw-axis. The intersections of the axes of these helixes with the basal plane form the unit basal triangles. This is the Sohncke point-system 23 or 24, the x-ray method being unable to make a decision between the two systems, which differ only in the direction of the screw. For the purposes of the demonstration given here it is immaterial whether the screw is right-handed or left-handed. The radius of the helix can be calculated from Bradley's data, and is 1.20 Å., representing the distance from the center of each atom to the axis of the helix.

There are thus two inter-atomic distances, namely, that between atoms in the same helix and that between atoms in different helixes. As Bradley showed for selenium it may be shown for tellurium also that the distance between nearest atom centers in the same helix is much less than that between atom centers in different helixes. For tellurium these values are 2.86 Å. and 3.46 Å., respectively. This doubtless means that the atoms in the same helix are held together by cohesive forces much greater than those binding atoms in different helixes, and that the crystal is "harder" in the direction of the screw-axis than perpendicular to it. Bradley has pointed out that the uniqueness of this axis, present in both selenium and tellurium, doubtless accounts for many of the directional properties observed in the two elements, and that crystallization is probably preferentially along this axis. This was found to be the case by Bridgman, who states that the trigonal (screw) axis lay longitudinally in the casting.

It is evident that this crystal structure is not closely packed, and it is conceivable that a change in either of the major dimensions, that of the side of the unit basal triangle, a, or that of the prism edge, h, should cause a change in density resulting merely from a difference in the closeness of the packing of the atoms, the two inter-atomic distances remaining unchanged. In such a process a lengthening of the prism edge h would cause a shortening of a and also a shortening of the radius of the helix. If such an elongation would result in an increase in density, it is entirely reasonable to suppose that an increase in pressure, tending towards an increase in density, would in fact cause a lengthening of this axis, with an attendant shortening of the other two dimensions. Such a lengthening would obviously cause the abnormal coefficient observed by Bridgman.

Fig. 2 shows a curve representing density as a function of the height of the unit prism. The values from which the curve was plotted were calculated by taking a series of values for h and keeping the inter-atomic distances, 2.86 Å. and 3.46 Å., unchanged, calculating the radius of the helix and the side of the unit basal triangle, *a*, and from these the density of the hypothetical crystal. The curve passes through a minimum at a density slightly greater than 6.20, corresponding to a value for *h* of 5.55 Å. For a prism of height less than 5.55 Å. an increase in pressure tending to cause an increase in density could do so only by shortening *h*, the two interatomic distances remaining unchanged, and the screw-axis would therefore show the usual positive compressibility coefficient. On the other hand, if the value for *h* lay to the right of 5.55 Å. an increase in pressure would cause a lengthening in *h*, since such a process would result in an increase in density. The actual value of *h* for tellurium, indicated by the arrow in the figure, is 5.91 Å. and is therefore to the right of the minimum, so that an increase in pressure should cause an increase in *h*, or, in other words, a negative compressibility coefficient along this axis.

Apparently no measurements have been made upon the compressibility of selenium along the screw-axis, but on the basis of the reasoning advanced here its behavior can be predicted. Fig. 3 is a curve for selenium similar to Fig. 2 for tellurium. The actual value for *h*, indicated by the arrow, appears to lie very slightly to the left of the minimum, and therefore the height of the unit prism would very likely decrease with the application of pressure (assuming, of course, that the lattice dimensions used in the calculations are correct); but since the screw-axis is in a state of greater compression than the triangular axes the compressibility along this axis is probably low.

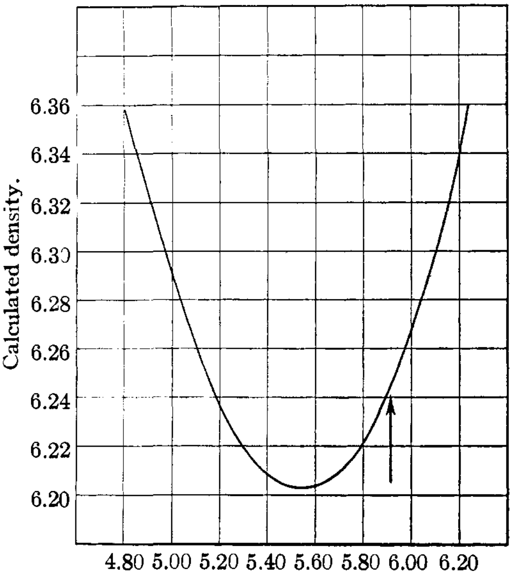

Fig. 2.—Tellurium.

Resisting the elongation (or contraction) of the helix upon the application of pressure, there is the tendency within the lattice to maintain the angle formed by any three atoms in the same helix at (for tellurium) 126.5°, and this tendency doubtless becomes more and more urgent as the angle departs further and further from this value, so that it may be assumed that the adjustment of density by the lengthening or shortening of the helix meets with increasing resistance as the pressure rises. It is this restraint which prevents the helix from straightening completely upon the first application of pressure.

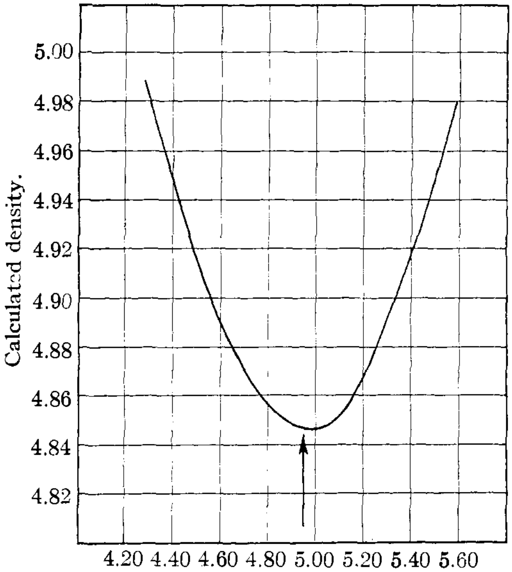

Fig. 3.—Selenium.

It is wholly possible, if the reasoning advanced here is valid, that other substances might be found to show negative coefficients of linear compressibility when the crystal structure permits an adjustment of packing similar to that in the case of tellurium. Structures such as those represented by the Sohncke point-systems 19 and 20, and 23 and 24, that is, possessing a screw-axis, should show this behavior when *h* is on the right (or left) of the minimum, though when the substance concerned is a chemical compound it is probable that the directive forces, presumably here much stronger than in the elementary state, might offer much greater resistance to the elongation of the screw-axis.

In conclusion the authors wish to express their indebtedness to Professor T. W. Richards for the use of the apparatus and also for the kindly interest he has taken in the work.

Summary

1. The average cubic compressibility of tellurium between 100 and 500 megabars and at 25° has been found to be 5.00×10^{-6}; the significance of this result has been discussed.

2. An approximate value has been found for the compressibility of water at 25°, namely, 41.54×10^{-6}.

3. The negative coefficient of linear compressibility observed by P. W. Bridgman has been explained and a prediction made concerning the behavior of selenium. It is pointed out that a negative linear compressibility is not denied by the principle of Le Chatelier and that under certain conditions might be observed in other substances.

Cambridge 38, Massachusetts