

On the Effect of Slight Impurities on the Elastic Constants, Particularly the Compressibility of Zinc

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The conclusion of Hanson that the elastic constants and particularly the compressibility of different grades of pure zinc differing only slightly in purity may differ by relatively large amounts is subjected to direct experimental test by compressibility measurements on the same grades of zinc as used by Hanson. Measurements on virgin material show no measurable difference. Apparent differences, both in compressibility and in the other elastic constants, are probably to be explained by small internal strains. Improved values are found for the compressibility of zinc as follows:

$$\begin{aligned} 90^\circ \text{ orientation,} & \quad -\Delta l/l_0 = 1.57 \times 10^{-7} p - 0.75 \times 10^{-12} p^2, \\ 0^\circ \text{ orientation,} & \quad -\Delta l/l_0 = 13.50 \times 10^{-7} p - 7.68 \times 10^{-12} p^2, \\ \text{Volume compression,} & \quad -\Delta V/V_0 = 16.64 \times 10^{-7} p - 9.62 \times 10^{-12} p^2, \end{aligned}$$

at 30°C, p in kg/cm².

IN the *Physical Review* for March 1, 1934, Hanson has published a careful determination by the method of the bending and twisting of cylindrical rods of the five elastic constants of zinc crystals from two different sources, both of purity higher than 99.99 percent, and has calculated from these constants the linear and cubic compressibilities. Considerable differences were found in some of these constants; for example, the calculated linear compressibility parallel to the axis of one grade of zinc was 40 percent higher than that of the other, and the cubic compressibility was 30 percent higher. These results were quite unexpected to me, both because of the opinion which seems to be quite widely held by experimenters on phenomena in crystals that the elastic constants are not "structure sensitive," and also because of my own personal experience. I had made measurements of the elastic constants by a more direct method and had found nothing to suggest as great a variability as found by Hanson. This was in particular true of my direct measurements of the linear compressibilities, which gave more clean cut results than for the other constants. Furthermore, all my experience with the compressibility of other materials indicated that it is not sensitive to slight impurity.

The matter seemed important to me, since our opinions on "structure sensitive" properties of crystals are still hardly out of the controversial stage, and it would be desirable to get this

matter correct in the beginning if possible. I therefore suggested to Professor Tyndall, under whose direction Hanson's work was done, the desirability of checking by direct experiment on the identical specimens some of Hanson's calculated compressibilities. Professor Tyndall cooperated in the readiest way by immediately placing at my disposal all of Hanson's samples of suitable orientation. Nine sets of measurements in my regular pressure apparatus were made on these samples. On consulting with Professor Tyndall as to the form which the results should take for publication, considerable difference of opinion developed as to the proper interpretation, and it eventually appeared after considerable correspondence that conclusions satisfactory to both of us could be obtained only by the execution of fresh experiments. The main point at issue hinged on the effect of the handling which the specimens had received, since they were known in some instances to have been strained beyond the elastic limit. The effect of this strain was removed as far as possible by a process of annealing which at that time was believed to be effective in restoring the electrical properties to the original condition, although there was no proof that the elastic properties were similarly restored, and it has developed later that even the electrical properties are not equally well restored at all orientations. Professor Tyndall therefore undertook the preparation of fresh samples of zinc especially for this work, and every

precaution has been taken to avoid all possibility of overstrain.

The freshly prepared zinc crystals were from three sources: (1) Evanwall "Rod" (E. R.) zinc made from material left by Hanson, originally obtained from the Evans Wallower Zinc Company; (2) Evanwall "Block" (E. B.) zinc from a fresh 50 pound block of zinc from the Evans Wallower Zinc Company, the same as the zinc used by Cinnamon¹ in a recent paper, and (3) Horsehead Special (H. H.) zinc, from the same 50 pound block as used by Hanson. Another sample of zinc from Evans Wallower showed by direct chemical analysis: Fe 0.0004 percent, Cd 0.0008 percent, Pb 0.0047 percent, Cu 0.0002 percent, As, Co, Ni, Al, 0.0000. Spectroscopic comparison of this with the E. R. zinc showed no detectible difference. Spectroscopic comparison with the H. H. zinc indicated somewhat more iron and somewhat less copper than the E. R. zinc. Spectroscopic comparison between E. R. and E. B. showed no iron at all in E. B. and slightly more copper. There were three samples of E. R. of orientations 5°, 90° and 8°, the angle being measured between the hexagonal axis of the crystal and the length of the rod. The 8° specimen had been strained in removing from the mold, and slip bands could be seen on the central portion, but the ends appeared free from slip bands. There were two samples of E. B. of orientations 9.5° and 85°. There were four samples of H. H. of 5°, 8°, 21°, and 89° orientations. The 21° orientation was really not pertinent for the present purpose, and was measured more or less by way of curiosity. These all were cast by methods already fully described² into crystals about 8 cm long and of slightly trapezoidal section about 5 mm on the side. For the compressibility measurements it was necessary to form these into pieces about 2.7 cm long for the more incompressible orientation and 1.3 cm long for the other more compressible orientation, with accurately flat and parallel ends. In order to perform the small amount of necessary machining, the specimens were first embedded in wax in a heavy brass tube of internal diameter just sufficient to admit the rod freely. The wax was cast around the rod

TABLE I. *Summary of linear compressibility measurements on fresh samples of zinc.*

Grade of zinc	Orientation	Linear compression at 30°		$-\Delta l/l_0$ at 10,000 kg/cm ²	Width of hysteresis loop	Average deviation from smooth curve
		$1.57 \times 10^{-7} p - 0.75 \times 10^{-12} p^2$	$-\Delta l/l_0$			
E. R.	90°			0.00149		1.90%
E. B.	85°			.00159		.83
H. H.	89°			.00151		.83
E. R.	5°	13.39	- 6.75	.01270	0.83%	.14
E. B.	9.5°	13.03	- 5.98	.01243	1.36	.50
H. H.	8°	13.56	-10.65	.01249	.75	.18
H. H.	5°	13.18	- 6.01	.01258	.83	.21
E. R. Strained	8°	12.71	- 7.45	.01197	1.27	.35
H. H.	21°	11.77	-10.35	.01073	1.40	.24

by slowly lowering the mold containing the crystal surrounded by molten wax into cold water by a process very similar to my method for making single crystals. Pieces were then cut out of the mold of the requisite length with a fine jeweller's saw; the ends of the specimen were faced off in the lathe while still embedded in the wax, taking a very fine chip and using a keen tool, and finally the completed specimen was freed from the mold by melting the wax. In a few cases there were longitudinal ridges left from the casting that had to be removed; this was done with a fine file, after part of the mold had been filed away, and while as much of the crystal as possible was still embedded in the wax.

The results of the measurements of linear compressibility of these fresh samples are given in Table I. The method was the same as in all my previous work and has been fully described.³ The measurements were made at 30°C, over a pressure range of 12,000 kg/cm², readings being made at equal pressure intervals with both increasing and decreasing pressure, making in all fourteen readings. The pressures in the tables are in kg/cm² units. In addition to the regular pressure run, an initial seasoning application of 2000 kg/cm² was made in all cases; this initial application was followed by no permanent change of zero within the regularity of the other readings, showing that there was no perceptible porosity in the specimen. The results could in practically all cases be represented within the regularity of the readings by a second degree expression in the pressure. Space does not permit a reproduction of all the individual readings, which repay careful

¹ C. A. Cinnamon, Phys. Rev. **46**, 215 (1934).

² W. J. Poppy, Phys. Rev. **46**, 815 (1934).

³ P. W. Bridgman, Proc. Am. Acad. **58**, 166 (1923).

study. The results were never entirely regular within the limits of error of the method, but there were irregularities greater than would be shown under similar conditions by harder materials. The most important feature was that there was always perceptible hysteresis between pressure and change of length for the most compressible orientation, that is, parallel to the axis, while the other and relatively incompressible orientation showed no appreciable hysteresis. In order to indicate the character of the results as fully as possible Table I contains, in addition to the two power expression in pressure which best represents the results, the maximum width of the hysteresis loop expressed as a fractional part of the total displacement at the maximum pressure, and the mean departure from a smooth curve of the individual points similarly expressed. This latter gives an idea of the regularity of the results; it will be seen that the average deviation is of the order of a few tenths of one percent. It is significant that by far the greater part of the average irregularity was contributed by the initial points at atmospheric pressure. A result of this would be that measurements made in only a small pressure range would show much greater irregularity, both relatively and absolutely, than measurements over a wider range. In order to eliminate as far as possible the effect of small local irregularities, I have chosen as giving the best comparative indication of the true compressibility the fractional change of length under 10,000 kg/cm². This change of length should be a linear function of $\cos^2 \theta$. The results are plotted in Fig. 1 against $\cos^2 \theta$ giving only the parts of the diagram on a much enlarged scale in the neighborhood of $\cos^2 \theta = 0$ and $\cos^2 \theta = 1$.

The diagram will leave no room for doubt, I believe, but that the linear compressibilities of these different grades of zinc are as close to the same value as could be expected in view of the experimental irregularity, and that no difference exists within experimental error which can be correlated with a difference in origin of the samples and therefore with minute differences in purity. The extreme discrepancy between any two samples is 1.2 percent, which is to be contrasted with a discrepancy of 40 percent in Hanson's averaged final results. This is the main

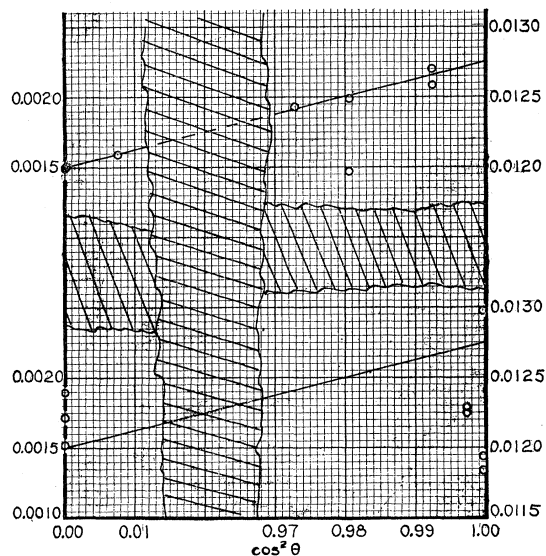


Fig. 1. Shows in the upper part of the diagram the fractional changes of length at 10,000 kg/cm² plotted against $\cos^2 \theta$ for the freshly prepared zinc crystals. In the lower part of the diagram are shown similar data for the elasticity samples of Hanson. Elasticity theory demands that the relation be linear in $\cos^2 \theta$.

point of this paper, and I believe establishes the fact that there is at present no reason to believe that at any rate the compressibilities are sensitive to small impurities.

It is instructive that the compressibility of the one sample known to have been strained in the mold, which is also plotted in Fig. 1 and which may be identified by comparison with Table I, definitely does not fall in line with the others, in spite of the fact that the sample was cut from what appeared to be an undamaged part of the crystal. This suggests the extreme sensitiveness of these effects to strain. Doubtless the fact that the individual readings for all the other samples were not as regular as those given by many other mechanically harder materials is to be explained as an effect of slight strains introduced in spite of the greatest care in handling.

The results listed in Table I for the 21° sample should be given no consideration in comparison with the others because the method is not adapted to measuring the linear compressibility of such an orientation. The thickness of this sample was about one-half its length; calculation will show that under hydrostatic pressure there is a change of angle for this orientation which in specimens of these proportions produces an effect

far from negligible, giving too low an apparent compressibility. In fact, the compressibility of this sample was too low by 5 percent.

It is now instructive to compare these results, obtained on virgin unstrained specimens, with the measurements made on the specimens which had been previously used by Hanson in determining the five elastic constants, and which were known in at least some cases to have been strained before the compressibility measurements. The results are given in Table II. They are distinctly more irregular than those for the virgin material in Table I. This is particularly evident in the second degree terms which in two instances have a positive sign, a very abnormal state of affairs indeed. The relative changes of length at 10,000 kg/cm² are plotted in the lower part of Fig. 1. The very much greater scattering of the points is in the first place striking and also the fact that at the high orientations all the points lie above the line for the unstrained material and at the low orientations all, with one exception, lie below it. The obvious interpretation of this is that small strains act effectively like the introduction of other orientations; at 90° the only other orientations possible are nearer 0°, and at 0° the only possible other orientations are nearer 90°.

Going back now to the results on the unstrained specimens, the present values of compressibility are much to be preferred to those which I previously published,⁴ not only is the

present material purer than mine, which we have seen to be of comparatively minor importance, but the specimens were doubtless freer from strain. The average values given by the new measurements, weighting measurements on different specimens inversely as their average deviations from a smooth curve, and correcting for orientation, are at 30°C pressure expressed in kg/cm²:

$$\begin{aligned} \text{At } 90^\circ, \quad -\Delta l/l_0 &= 1.57 \times 10^{-7} p - 0.75 \times 10^{-12} p^2. \\ \text{At } 0^\circ, \quad -\Delta l/l_0 &= 13.50 \times 10^{-7} p - 7.68 \times 10^{-12} p^2. \end{aligned}$$

From these the volume compressibility may be computed to be:

$$-\Delta V/V_0 = 16.64 \times 10^{-7} p - 9.62 \times 10^{-12} p^2.$$

My previous results were:

$$\begin{aligned} \text{At } 90^\circ, \quad -\Delta l/l_0 &= 1.95 \times 10^{-7} p - 1.11 \times 10^{-12} p^2. \\ \text{At } 0^\circ, \quad -\Delta l/l_0 &= 12.98 \times 10^{-7} p - 5.32 \times 10^{-12} p^2. \\ \text{Cubic, } -\Delta V/V_0 &= 16.87 \times 10^{-7} p - 8.08 \times 10^{-12} p^2. \end{aligned}$$

It will be noticed that the difference between the two determinations is in exactly the direction that would be expected, that is, the linear compressibility of the strained 90° specimen is greater than that of the unstrained specimen, because of the effective introduction by the strain of other orientations, all of which have a greater compressibility, while for the 0° orientation the relations are reversed. The result is a comparatively large change in the ratio of the compressibilities in the two directions, the ratio being 8.6 for the unstrained specimen and only 6.65 for the strained specimen. It is also to be noticed that the effect of strain is much larger on the 90° orientation, measured in percent, than on the 0° orientation; the absolute magnitudes of the effects are not greatly dissimilar.

Interesting questions suggest themselves as to the mechanism by which strain simulates the effect of a change of orientation. The cleavage planes seem to be unchanged in orientation and as easily produced in strained as in virgin specimens. Perhaps the possibility is to be considered of a partial rotation of the atoms in position in the lattice; it is probable that the atoms cannot have complete spherical symmetry in a lattice as strongly anisotropic as zinc. The fact that annealing is comparatively successful in restoring electrical properties is not incon-

TABLE II. Summary of linear compressibility measurements on Hanson's elasticity samples.

Grade of zinc	Orientation	Linear compression at 30° -Δl/l ₀	-Δl/l ₀ at 10,000 kg/cm ²	Width of hysteresis loop	Average deviation from smooth curve
E. R. b.a.	90°	1.38 × 10 ⁻⁷ p + 3.38 × 10 ⁻¹² p ²	0.00172		1.18%
E. R. a.a.	90°	1.96 - 0.70	.00189		1.86
H. H. a.a.	90°	1.49 + 0.33	.00152		.68
E. R. b.a.	3°	13.91 - 16.55	.01225	1.7%	.13
E. R. a.a.	3°	13.60 - 13.1	.01229	2.1	.25
H. H. b.a.	1°	13.40 - 4.22	.01298	.45	.09
H. H. a.a.	1°	12.98 - 10.40	.01194	2.1	.28
H. H. a. 2nd a.	1°	12.91 - 10.72	.01184	1.8	.29

b.a., before annealing, or "as received."
a.a., after annealing, 380° for 8 to 10 hours.
a. 2nd a., second annealing, 400° for 24 hours.

⁴ P. W. Bridgman, Proc. Am. Acad. 60, 338 (1925).

sistent with an asymmetry in the atoms because the wave mechanics picture of electrical conduction represents the electron distribution as much more uniform than the atomic distribution. This is also suggested by the fact that the ratio of the electrical conductivities for the two independent perpendicular directions is only 1.055, against 8.6 for the ratio of the elastic constants.

Leaving now the question of compressibility and passing to the other elastic constants as determined by Hanson, it seems to me that one may well question whether there is any longer ground to believe seriously that the other constants are sensitive to minute impurities. For I think it may be taken as now established that there is no such variation in the compressibility as Hanson calculated from his other constants and this of course means an error in those constants. There are two factors which I think should be especially considered in appraising the situation. There is in the first place the consideration that slight permanent strains may introduce *systematic* errors, changing the elastic properties for orientations near one extreme all in one direction, and those near the other extreme in the other. In the second place, there is the consideration that slight errors in the observational data may, because of the nature of the mathematical relationships, introduce very serious errors into some of the computed elastic constants. Thus it can be shown that by making a change of only 1 percent in the direct observational data from which S_{11} , S_{33} and S_{44} are computed, a change of 18 percent may be thereby introduced into S_{12} , 22 percent into S_{13} , 35 percent into the parallel linear compressibility, 81 percent into the perpendicular linear compressibility, and 47 percent into the cubic compressibility. If one examines the regularity of the experimental points in Hanson's diagrams, and further considers the possibility of systematic errors just mentioned and the fact that all the bending specimens consistently showed distinct hysteresis, I believe that the danger of an accumulation of errors like that just suggested must appear to be a very real one.

The possibility of systematic errors arising from small strains offers the possibility of understanding how Hanson could have arrived at his

conclusion that very small differences in purity produce comparatively large differences in elastic constants. For the elastic limit is known to be sensitive to very slight impurities so that one grade of zinc may have been more susceptible to permanent strain than the other, and therefore more sensitive to systematic error. Something of this sort is definitely suggested by a study of the irregularities of the data. The spectroscopic analysis suggests that the H. H. zinc was slightly less pure than E. R. or E. B. and therefore less likely to receive permanent strains. Tables I and II both show a distinct tendency for the H. H. points to deviate less from smooth curves than the others which is what would be expected. There is also the fact that the compressibilities calculated by Hanson for the H. H. zinc are distinctly nearer the values directly determined above than are the others.

In view of the various possibilities of error in the method of determination of elastic constants by bending and torsion, particularly when applied to substances with low elastic limits, it is pertinent to urge the great superiority of "direct" methods, that is, methods in which the specimen is subject to a homogeneous stress and strain corresponding to the constant to be determined. The constants S_{11} and S_{33} can be measured "directly" in terms of the shortening under compressive load, and so determined can be given more confidence than can be given to a determination by bending which involves a strain varying from positive to equal negative values across the section of a slender specimen. Similarly S_{12} and S_{13} can be determined by direct measurements of the lateral contraction of suitably oriented specimens, and so determined are not susceptible to the possibility of large accumulated errors already indicated in the indirect method. Finally there can be no doubt but that directly measured compressibilities are to be preferred to compressibilities calculated by a combination of other constants.

In a note following this Professor Tyndall presents the values of the elastic constants of zinc which he now thinks may be deduced with greatest probability from Hanson's data in view of these results on linear compressibility.