

# Elastic Properties of Zinc: A Compilation and a Review

H. M. Ledbetter

*Cryogenics Division, National Bureau of Standards, Boulder, Colorado 80302*

The elastic constants of zinc are compiled and reviewed; one hundred references are cited. The included elastic constants are: Young's modulus, shear modulus, bulk modulus, compressibility, Poisson's ratio, second-order single-crystal elastic stiffness and compliances, and third-order elastic stiffness. Temperature and elastic-anisotropy effects are also reviewed. Other topics are: sound velocities, elastic Debye temperature, Cauchy relationships, elastic stability, pressure effects, and theoretical studies. New polycrystalline data are computed from single-crystal data by tensor-averaging methods.

Key words: Bulk modulus; compressibility; Debye temperature; elastic constants; Poisson's ratio; shear modulus; single-crystal elastic coefficients; sound velocities; Young's modulus; zinc.

## Contents

	Page		Page
1. Introduction .....	1181	11. Polycrystalline Elastic Constants Computed from Single-Crystal Data .....	1195
2. Zinc as a Metal .....	1181	12. Temperature Dependence of Polycrystalline Elastic Constants .....	1196
3. Hexagonal Elastic Symmetry .....	1182	13. Sound Velocities .....	1196
4. Strains Associated with Elastic Constants ....	1184	14. Elastic Debye Temperature .....	1198
5. Experimental Second-Order Single-Crystal Elastic Constants .....	1184	15. Third-Order Elastic Constants .....	1199
6. Temperature Dependence of Second-Order Single-Crystal Elastic Constants .....	1187	16. Pressure Derivatives .....	1199
7. Elastic Anisotropy .....	1189	17. Theoretical Studies .....	1200
8. Elastic Stability .....	1192	18. Miscellaneous Topics .....	1201
9. Central Forces .....	1194	19. Conclusions and Recommendations for Further Studies .....	1201
10. Experimental Polycrystalline Elastic Constants	1194	20. References .....	1201

## 1. Introduction

Previous reports in this series discussed elastic properties of iron, nickel, and iron-nickel alloys [1]<sup>1</sup> and copper [2]. Reference 1 also discusses some solid-state elasticity concepts that are relevant here, including: crystal physics and thermodynamics; temperature effects; relationships between elastic constants and other physical properties, especially the elastic Debye temperature; and relationships between single-crystal and polycrystal elastic constants.

The purpose here is to present a compilation and a review of elastic properties of zinc. One hundred scientific and engineering publications are cited. Both single-crystal and polycrystal elastic constants are considered together with effects of familiar metallurgical variables on the constants.

Zinc is used widely technologically. Some better-known applications include: galvanized iron and steel, die cast-

ings, solders, and alloys. Brasses (zinc-copper alloys) are perhaps the best-known and most useful zinc alloys. Properties and applications of both zinc and its alloys are summarized elsewhere [3].

The first reasonably comprehensive review of anisotropic elastic-constant measurements, by Hearmon [4] in 1946, cited only three hexagonal metals: cadmium, magnesium, and zinc. But, hexagonal-metal elastic-property studies have proliferated in recent years. Hearmon's [5] more recent review in 1969 cites sixteen hexagonal metals. Except for magnesium, and perhaps beryllium, zinc has received more experimental study than other hexagonal metals. Magnesium has been studied extensively theoretically because its axial ratio is nearly ideal and because it is nearly elastically isotropic. As discussed below, a non-ideal axial ratio and a high elastic anisotropy make zinc studies more interesting but also more difficult.

## 2. Zinc as a Metal

Zinc seems at first to be a relatively simple metal with a relatively low atomic number (thirty). Its electronic

<sup>1</sup> Figures in brackets indicate literature references at the end of this paper.

Copyright © 1977 by the U.S. Secretary of Commerce on behalf of the United States. This copyright will be assigned to the American Institute of Physics and the American Chemical Society, to whom all requests regarding reproduction should be addressed.

structure,  $[\text{Ar}]3d^{10}4s^2$ , indicates that the  $d$  band is filled and that complicated  $d$ -band/ $s$ -band electronic interactions are possibly absent. Being diamagnetic, the properties of zinc do not depend on magnetic field. Its crystal structure is close-packed hexagonal (space group =  $D_{6h}^4 = P_{6_3}^{22} / \text{mmc}$  = no. 194 = structurbericht type A3). Between zero temperature and melting (692 K), zinc exhibits only one crystal structure; thus, its solid-state properties exhibit no unexpected discontinuities with temperature changes.

Further scrutiny shows that zinc is not a simple metal; its complexities include:

(1) Crystal structure. A pseudopotential calculation by Harrison [6] predicted that f.c.c. zinc has a lower energy than c.p.h. zinc, contrary to fact. A similar calculation predicted correct crystal structures for aluminum and beryllium, metals essentially as complicated as zinc. In pseudopotential formulations of metallic cohesion, the total energy is factored into electrostatic, band-structure, free-electron (Fermi), and correlation energies; only the first two depend on crystal structure. Calculations are done for zero temperature and do not, therefore, consider entropy in the phase-stability problem.

Offsetting this prediction, Kaufman [7] predicted that c.p.h. zinc is the most stable phase, but that it would transform to b.c.c. at 1125 K and to f.c.c. at 1250 K if melting did not intervene. Kaufman's model is based on separating thermodynamic functions (free energy, enthalpy, entropy, etc.) into lattice, electronic, magnetic, etc. parts, which are evaluated from experimental measurements. This analysis assumes the additivity of corresponding-states specific heats.

(2) Axial ratio. Hexagonal crystals that are most closely, or ideally, packed have a  $c/a$  ratio of  $(8/3)^{1/2} = 1.633$ . The ratio of zinc, 1.856, deviates considerably from ideal. Several attempts have been made to account for this unusually high axial ratio. The most convincing may be the pseudopotential calculation of Weaire [8] that showed the band-structure energy is a minimum when  $c/a = 1.8$ . A similar calculation gave nearly correct axial ratios for beryllium, cadmium, mercury, and magnesium. It follows from the axial ratio that the intra-basal-plane interatomic bonds are stronger than the inter-basal-plane bonds. The basal cleavage of zinc and its higher compressibility perpendicular to the basal plane substantiate this. In terms of atomic packing, zinc atoms should be considered oblate spheroids rather than spheres. The atomic packing of zinc indicates the possibility of covalent, or angular, bonding. However, Hume-Rothery [9] maintained that the valence and crystal structure of zinc cannot be rationalized by a tendency toward covalency.

Thus, theoretical understanding of the stable crystal structure and axial ratio of zinc is incomplete. A factor in all these properties is  $s$ - $p$  hybridization. As discussed by Dehlinger [10], the symmetry of the wave function must be reconciled with the point-group symmetry; and this reconciliation affects the spacing, packing, arrangement, and energy of atoms in crystals. Dehlinger discussed

zinc in terms of hybrid  $s$ - $p$  wave functions that are aligned preferentially along the close-packed directions in the basal plane. As described below, the elastic behavior of zinc is also unusual; and usual theoretical models fail to describe its elastic properties.

### 3. Hexagonal Elastic Symmetry

From an elastic viewpoint, zinc is relatively complicated. To better understand the elasticity of zinc a few basic concepts are outlined. Further details can be found in Nye [11], Fedorov [12], and Musgrave [13]. The coordinate system used to describe the elastic constants in the present paper is shown in figure 1.

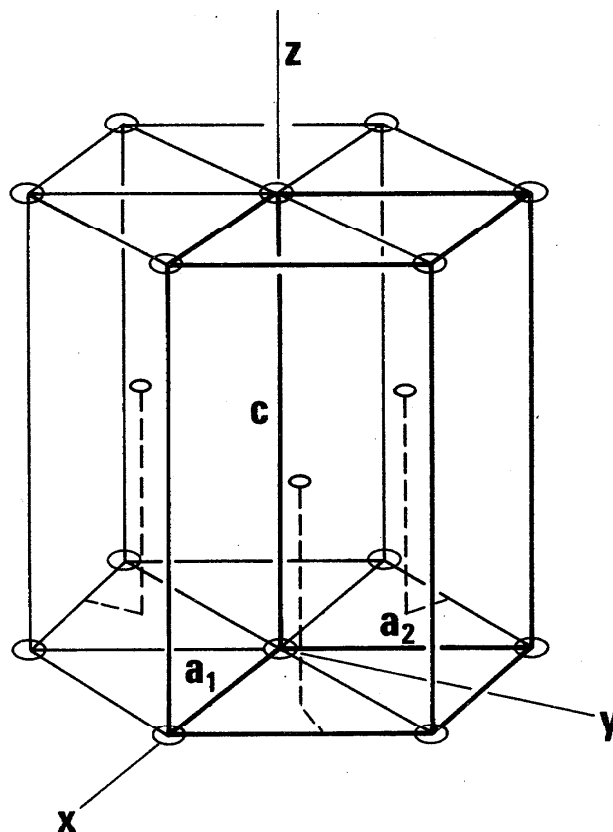


FIGURE 1. Schematic diagram of a close-packed hexagonal unit cell defined by  $a_1$ ,  $a_2$ , and  $c$ . The orthogonal co-ordinate system used in this paper is denoted by  $x$ ,  $y$ , and  $z$ .

Materials that are either isotropic or quasi-isotropic have only two independent elastic constants. By quasi-isotropic is meant a material that is macroscopically isotropic but microscopically anisotropic; polycrystalline aggregates of single crystals are good examples of quasi-isotropic materials. When a body is stressed below its elastic limit, its shape and volume change reversibly. The strain,  $\epsilon$ , is related to the stress by Hooke's law,  $\epsilon = S\sigma$ , where  $S$  is the elastic compliance; or alternatively the stress is related to the strain by  $\sigma = C\epsilon$ , where  $C$  is the elastic stiffness; and  $C$  and  $S$  are inverses.

Depending on symmetry, a crystal has up to twenty-one independent second-order elastic constants. Hooke's law for single crystals is

$$\sigma_{ij} = C_{ijkl}\epsilon_{kl}, \quad (1)$$

where  $\sigma_{ij}$  and  $\epsilon_{kl}$  are the second-rank stress and strain tensors and  $C_{ijkl}$  is the fourth-rank elastic-stiffness tensor. If the crystal has some elastic symmetry, then the number of independent  $C_{ijkl}$ 's is less than twenty one. In eq (1) the usual rule of omitting the summation symbol is adopted; summation over the values 1, 2, 3 is implied by all suffixes that occur twice in a term.

Hexagonal crystals have five independent elastic constants. The elastic stiffnesses are displayed in eq (2) in the Voigt contracted notation in matrix form:

$$C_{ij} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & \frac{1}{2}(C_{11} - C_{12}) \end{bmatrix} \quad (2)$$

where the matrix is symmetrical about its main diagonal, that is  $C_{ij} = C_{ji}$ . Equation (2) results simply from the existence of a six-fold rotation axis; the additional symmetry elements indicated above by the space group effect no further elastic-symmetry simplifications. Only one independent elastic constant,  $C_{44}$ , appears in the  $C_{ij}$  matrix.

If this matrix is inverted to obtain the  $S_{ij}$ 's, the elastic compliance coefficients, then these can be related to the so-called practical elastic constants:  $E$  = Young's modulus,  $G$  = shear modulus, and  $\nu$  = Poisson's ratio as displayed in the matrix equation:

$$S_{ij} = \begin{bmatrix} 1/E_{11} & -\nu_{21}/E_{11} & -\nu_{31}/E_{33} & 0 & 0 & 0 \\ & 1/E_{11} & -\nu_{31}/E_{33} & 0 & 0 & 0 \\ & & 1/E_{33} & 0 & 0 & 0 \\ & & & 1/G_{44} & 0 & 0 \\ & & & & 1/G_{44} & 0 \\ & & & & & \frac{2}{E_{11}}(1+\nu_{21}) \end{bmatrix} \quad (3)$$

where the Poisson ratios are given by

$$\nu_{ij} = -S_{ij}/S_{ii} \text{ (no sum)}. \quad (4)$$

If interatomic forces are central (independent of angle), if ions are at centers of symmetry, and if the crystal is stress free, then the following relationships occur among the  $C_{ij}$ 's:

$$C_{12} = C_{66} = \frac{1}{2}(C_{11} - C_{12}), \text{ or } C_{11} = 3C_{12}, \quad (5)$$

and

$$C_{13} = C_{44}. \quad (6)$$

These are called the Cauchy relationships. For central forces, the  $C_{ij}$  matrix becomes

$$C_{ij} \text{ (central-force)} = \begin{bmatrix} C_{11} & \frac{1}{3}C_{11} & C_{44} & 0 & 0 & 0 \\ & C_{11} & C_{44} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & \frac{1}{3}C_{11} \end{bmatrix} \quad (7)$$

If a hexagonal crystal is elastically isotropic, all elastic constants have the same values in all directions. Then the following relationships hold among the  $C_{ij}$ 's:

$$C_{66} = \frac{1}{2}(C_{11} - C_{12}) = C_{44}, \quad (8)$$

$$C_{12} = C_{13}, \quad (9)$$

and

$$C_{11} = C_{33}. \quad (10)$$

Thus, for an isotropic hexagonal crystal the  $C_{ij}$  matrix is

$$C_{ij} \text{ (isotropic)} = \begin{bmatrix} C_{11} & C_{11} - 2C_{44} & C_{11} - 2C_{44} & 0 & 0 & 0 \\ & C_{11} & C_{11} - 2C_{44} & 0 & 0 & 0 \\ & & C_{11} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{44} \end{bmatrix} \quad (11)$$

with two independent elastic constants.

For the case of both central forces and elastic isotropy, the  $C_{ij}$  matrix is

$$C_{ij} \text{ (central-force, isotropic)} = C_{11} \begin{bmatrix} 1 & \frac{1}{3} & \frac{1}{3} & 0 & 0 & 0 \\ & 1 & \frac{1}{3} & 0 & 0 & 0 \\ & & 1 & 0 & 0 & 0 \\ & & & 1 & 0 & 0 \\ & & & & 1 & 0 \\ & & & & & 1 \end{bmatrix} \quad (12)$$

with only one independent elastic constant.

#### 4. Strains Associated with Elastic Constants

Crystalline elastic properties are more easily understood from physical or geometrical models that relate the strain response of a body to an applied load. These models can be summarized by linear combinations of the  $C_{ij}$ 's that correspond to different strains. These strains cannot be chosen uniquely. The following set has proven useful.

There are three independent ways to deform a hexagonal crystal and conserve its volume.

(1)  $\frac{1}{2}(C_{11} - C_{12})$ . This strain deforms the equilateral hexagonal unit-cell base so that its area is unchanged, but angles between base vectors are changed. The  $c$  axis is unaffected.

(2)  $C_{44}$ . This strain shears on the basal plane, leaving the basal plane unaffected but tilting the  $c$  axis with respect to the basal plane.

(3)  $C = \frac{1}{6}(C_{11} + C_{12} + 2C_{33} - 4C_{13})$ . This strain compresses (stretches) the  $c$  axis and at the same time expands (contracts) the basal plane uniformly by an amount such that volume is conserved. Thus, symmetry is unaffected but axial ratio is changed.

In hexagonal lattices there is one deformation that dilates uniformly:

(4)  $B = \frac{1}{9}(2C_{11} + C_{33} + 2C_{12} + 4C_{13})$ . This strain amounts to expanding or contracting all vectors uniformly so that the  $c/a$  ratio is invariant and the basal plane retains its equilateral hexagonal shape. No shears are involved in this strain.

The symmetry condition  $C_{66} = \frac{1}{2}(C_{11} - C_{12})$  has an important consequence in hexagonal crystals.  $C_{66}$  is the shear constant on the (100) plane in a [010] direction, while  $\frac{1}{2}(C_{11} - C_{12})$  is the shear constant on the (110) plane in a [ $\bar{1}10$ ] direction. Thus, the elastic shear constant for all planes in the [001] zone is the same, independent of the particular shear plane or shear direction. This condition is called transverse isotropy. It means the elastic constants are invariant to arbitrary rotations around the  $z$  axis; in the  $xy$  plane, hexagonal crystals are elastically isotropic.

At first, it appears that hexagonal materials, with five independent elastic constants, are more complicated than cubic materials, with three independent elastic constants. In most cases, this is wrong. For example, Lifshitz and Rosentzweig [14] gave a closed-form solution for the elastic Green's tensor in hexagonal crystals; for cubic crystals they gave a closed-form solution only in the limit of elastic isotropy. Similarly, Pynn [15] gave an exact analytic expression for the elastic Debye temperature of hexagonal crystals; for cubic crystals, an iterative, a series-expansion, or an approximationsal method must be used.

#### 5. Experimental Second-Order Single-Crystal Elastic Constants

The second-order single-crystal elastic constants of zinc are given in tables 1 and 2 for the  $S_{ij}$ 's and the  $C_{ij}$ 's, respectively. All data known to be reported in the literature are included in the tables together with some useful derived quantities. Reported  $S_{ij}$ 's were converted to  $C_{ij}$ 's, and vice versa, by matrix inversion. Recommended values are also given in the tables; they were obtained by averaging arithmetically, without weighting, the data for all representative specimens. All data were included in the averages except outlying observations, which were identified by deviations of greater than  $1.5\sigma$ , where  $\sigma$  is the usual standard deviation based on an assumed normal distribution. Discarded, or outlying, values are indicated by parentheses; and they were not included in either the average values or in the standard deviations. The percentage uncertainties given in the tables are the standard deviation divided by the average value times one hundred. This is a useful uncertainty statement except when the elastic constant is near zero, as in the case of  $S_{12}$  for example.

Zinc has been an interesting subject in experimental elasticity. It was the first hexagonal metal for which the complete set of second-order elastic constants, the  $S_{ij}$ 's, was determined. The pioneering study by Grüneisen and Goens [16] in 1924 was made possible by their preparing sufficiently large oriented single crystals by "seeding." Large crystals facilitate lateral-strain measurements. Most previous studies on zinc used specimens prepared from compacted powders. Their study was the first of its type following Voigt's [17] classic studies. Excluding some previous studies on copper, the Grüneisen and Goens study represents the first complete study of the single-crystal elastic constants of a metal. Their object was to determine the Debye-characteristic-frequency limits, which determine specific heat, thermal expansion, and other properties. Their study is also unique in being the first description of the velocity of sound in a hexagonal crystal. Two experimental methods were used. Young's modulus was measured in transverse oscillation to reduce the risk of plastically deforming the zinc crystals. The torsional modulus was determined in a static torsional experiment using mirrors on the specimen to amplify the strain. Grüneisen and Goens were also first to use vibrational methods on non-cubic crystals. Perhaps the most striking result of the Grüneisen and Goens study is the exceptionally large ratio of  $K_{\parallel}$  to  $K_{\perp}$ , the linear compressibilities parallel and perpendicular to the six-fold axis. As shown in figure 15,  $K_{\parallel}/K_{\perp}$  is about 8 for zinc. This is extraordinary since, for example, the ratio of electrical resistivity parallel and perpendicular to the six-fold axis is only 1.05. As shown in table 1, their experimental results, obtained about fifty years ago, basically agree with the best recent results.

TABLE 1. Single-crystal second-order elastic-compliance coefficients of zinc at room temperature; units are  $10^{-11}$  m<sup>2</sup>/N. Values in parentheses were discounted as outlying observations.

Source	$S_{11}$	$S_{33}$	$S_{44}$	$S_{22}$	$S_{13}$	$S_{66}$	$K_{\parallel}$	$K_{\perp}$	K	$2S_{13} + S_{44}$	Experimental method
Grüneisen, Coens [16]	0.80	2.82	2.50	(-0.05)	-0.605	(1.70)	(1.61)	0.145	1.90	1.290	Static: extension & torsion Dynamic: resonance
Bridgman [18, 68]	0.823	2.638	2.500	0.034	-0.564	1.578	1.298	0.195	1.687	1.172	Static: extension, compression & torsion
Goens [19]	0.84	2.87	(2.64)	0.11	-0.775	1.46	1.320	0.175	1.670	1.09	Static: bending & torsion Dynamic: resonance
Hanson [20]	0.808	2.623	2.515	(0.157)	(-0.785)	(1.302)	(1.058)	0.180	(1.418)	(0.945)	Static: bending & torsion; Evanwall zinc
Hanson [20]	(0.770)	2.766	2.440	0.045	-0.639	1.450	1.488	0.176	1.840	1.162	Static: bending & torsion; Horsehead zinc
Bridgman [21]	(0.770)	2.766	2.440	0.083	-0.693	1.374	1.377	0.160	1.697	1.054	Static: compression Analysis of Hanson & Bridgman data
Tyndall [22]	(0.770)	2.766	2.440	0.083	-0.693	1.374	1.380	0.160	1.700	1.054	Static: compression Analysis of Hanson & Bridgman data
Read [23]	0.835	2.85								1.13	Dynamic: resonance
Bridgman [69]	0.838	2.838	2.61	0.053	-0.731	1.57	1.377	0.160	1.631	1.146	Static: pressure piston Static: extension & torsion & bending
Wert, Tyndall [24]	0.838	2.838	2.61	0.053	-0.731	1.57	1.377	0.160	1.696	1.146	Static: extension & torsion & bending
Alers, Neighbors [25]	0.841	2.823	2.578	0.055	-0.747	1.572	1.329	0.148	1.625	1.082	Dynamic: resonance, $K_{\parallel}$ and $K_{\perp}$ from Bridgman
Waterman [26]	0.795	(2.541)	2.597	0.005	-0.616	1.580	1.309	-0.184	1.677	1.365	Derived from $C_{ij}$
Musgrave [23]	0.826	2.748	2.500	0.033	(-0.567)	1.587	1.614	(0.292)	(2.198)	1.366	Derived from $C_{ij}$ , avg. value of $C_{ij}$ used Dynamic
Average values	0.823	2.775	2.520	0.052	-0.684	1.521	1.388	0.168	1.712	1.164	
Standard deviations	0.018	0.085	0.063	0.032	0.063	0.081	0.102	0.016	0.088	0.131	
Percentage uncertainties	2	3	3	62	9	5	7	10	5	11	

TABLE 2. Single-crystal second-order elastic-stiffness coefficients of zinc at room temperature, units are  $10^{11}$  N/m<sup>2</sup>. Values in parentheses were discounted as outlying observations. In this table,  $B = \frac{1}{9} \sum_{i,j=1,3} C_{ij}$ .

Source	$C_{11}$	$C_{33}$	$C_{44}$	$C_{12}$	$C_{13}$	$C_{66}$	$B$	Experimental method
Grüneisen, Goens [16]	1.608	0.542	0.400	(0.431)	0.437	(0.588)	0.708	Derived from $S_{ij}$ 's
Bridgman [18, 68]	1.590	0.621	0.400	0.323	0.482	0.634	0.708	Derived from $S_{ij}$ 's
Goens [19]	1.626	0.623	0.379	0.256	0.508	0.685	0.713	Derived from $S_{ij}$ 's
Hanson [20]	(1.776)	(0.740)	0.398	0.240	(0.602)	(0.769)	(0.798)	Derived from $S_{ij}$ 's
Hanson [20]	1.625	0.553	0.410	(0.171)	0.415	0.690	0.645	Derived from $S_{ij}$ 's
Tyndall [22]	1.716	0.610	0.410	0.261	0.495	0.728	0.727	Derived from $S_{ij}$ 's
Wert, Tyndall [24]	1.609	0.610	0.383	0.335	0.501	0.637	0.722	Derived from $S_{ij}$ 's
Alers, Neighbors [25]	1.637	0.635	0.388	0.364	0.530	0.636	0.751	Dynamic: pulse
Waterman [26]	1.628	0.627	0.385	0.362	—	0.633	0.693*	Dynamic: pulse, *avg. value of $C_{13}$ used
Musgrave [28]	(1.430)	(0.500)	0.400	(0.170)	(0.330)	0.630	(0.558)	Dynamic: pulse
Average values	1.630	0.603	0.394	0.306	0.481	0.659	0.708	
Standard deviations	0.038	0.035	0.011	0.052	0.041	0.037	0.031	
Percentage uncertainty	2	6	3	17	9	6	4	

Bridgman [18] independently reported the elastic constants of zinc. Except for the sign of  $S_{12}$ , his measurements agree reasonably well with the Grüneisen and Goens values. Subsequent measurements showed that Bridgman's positive  $S_{12}$  is correct, even though this is distinctly abnormal. All other hexagonal metals for which single-crystal elastic constants have been reported have negative  $S_{12}$  values. In the sense of Bridgman,  $S_{12}$  is a "rectangular" constant relating the stress perpendicular to the  $x$  plane to the strain perpendicular to the  $y$  plane, or vice versa. Hooke's law in this case is

$$\epsilon_1 = S_{12}\sigma_2. \quad (13)$$

For zinc, the Poisson ratio defined by

$$\nu_{12} = -\frac{S_{12}}{S_{11}} = -\frac{\epsilon_2}{\epsilon_1} \quad (14)$$

is negative. Physically, this means a tensile stress along the  $y$  axis causes an elastic expansion along the  $x$  axis, contrary to the usual situation where all directions perpendicular to the tensile axis are contracted. Since  $S_{13} = S_{23}$  is negative, the Poisson ratio  $\nu_{13}$  is positive and the strain  $\epsilon_2 = -\nu_{32}\epsilon_3 = -\nu_{23}^{-1}\epsilon_3$  is a contraction, as is typical. Bridgman believed his more direct measurements were better than those of Grüneisen and Goens, who used only two measurement modes on differently oriented rods: extension and torsion. Their  $S_{ij}$ 's were computed to best describe the  $S_{ij}$  orientation dependence.

Stimulated by Bridgman's results, Goens [19] reconsidered the second-order elastic constants of zinc, particularly concerning  $S_{12}$ 's sign. All previous measurements by Grüneisen and Goens were repeated, a new specimen was added, and the torsion-bending coupling problem was accounted for in the torsion experiments. Much better agreement was achieved among the torsion data, and new  $S_{ij}$ 's were proposed, as shown in table 1. However, agreement with Bridgman's results was hardly improved, except

for  $S_{12}$ 's sign. In adjusting his data, Goens matched his measurements along symmetry axes, where torsion-bending effects don't occur, to Bridgman's  $K_{II}$  and  $K_{\perp}$  values, which were considered especially accurate. Another difficulty with the Grüneisen-Goens crystals is that they were drawn from a melt; thus, they were neither perfectly circular nor uniform in cross section. Goens was the first to realize that in static experiments on zinc stresses due to handling and testing can exceed its yield stress. Goens's contribution to the torsion-bending coupling problem is especially significant, and it has stimulated many subsequent studies.

Believing that the scatter among the results of Grüneisen and Goens, Bridgman, and Goens required further study, Hanson [20] performed bending and torsional tests on differently oriented cylindrical rods of two grades of "pure" zinc. Significant differences were found in the elastic constants, as shown in table 1. Hanson believed these differences were real, that they reflected small variations in the amounts and kinds of impurities, and that they did not result from experimental or treatment errors. This astonishing conclusion contradicted the general belief that elastic constants are "structure insensitive," relatively unaffected by either chemical impurities or mechanical deformation.

Bridgman [21] tested Hanson's hypothesis by measuring the compressibility of both grades of zinc tested by Hanson. As shown in table 1, Hanson's compressibilities differed by about forty percent. Hanson's specimens were given to Bridgman, and some new specimens were prepared from the same stock materials. Bridgman found no difference in the compressibilities and concluded that Hanson's measurements contained large errors. Bridgman suggested two error sources: a systematic experimental error due to specimen strains, and error accumulation in computation. As pointed out by Bridgman, in Hanson's experiment the variable interconnectivity is such that a one percent error in  $S_{11}$ ,  $S_{33}$ , or  $S_{44}$  gives an eighteen percent error in  $S_{12}$ , a twenty-two percent error in  $S_{13}$ ,

an eighty-one percent error in  $K_{II}$ , and a forty-seven percent error in  $K$ . Bridgman's specimen-strain argument was supported by the fact that Hanson's data for the highest-impurity-content zinc, which would have a higher yield stress and, therefore, the lowest plastic strain due to handling and treatment, agreed best with other reported data. Bridgman again advocated for materials with low yield stress that "direct" methods should be used and bending experiments should be avoided.

Tyndall [22] attempted to salvage the situation for Hanson, who was Tyndall's student. Hanson's hypothesis concerning composition sensitivity was abandoned. Tyndall proposed new, self-consistent  $S_{ij}$ 's based on Hanson's and Bridgman's measurements and called them a "more satisfactory set of constants than any previously proposed." The Grüneisen and Goens data were neglected because "their measurements were made in part by a dynamic method." As shown in table 1, Tyndall should not have neglected their data; their  $S_{ij}$ 's are closer to the best values than are the  $S_{ij}$ 's proposed by Tyndall.

In an internal-friction study on zinc, Read [23] measured three of the elastic constants of zinc by a resonance composite-oscillator method. His values agree almost exactly with the best values given in table 1.

Wert and Tyndall [24] reported a twenty-five-crystal study using both static and dynamic methods, a departure from Tyndall's viewpoint concerning the validity of dynamic measurements. These results agree most clearly with those reported by Read [23] and by Goens [19]. Wert and Tyndall also used Bridgman's [21]  $K_{II}$  and  $K_I$  values to fill out their set of  $S_{ij}$ 's.

In 1958, three independent ultrasonic pulse experiments on zinc were reported. The  $C_{ij}$ 's, rather than the  $S_{ij}$ 's were determined directly for the first time. Alers and Neighbors [25] reported a complete set of  $C_{ij}$ 's between 4 and 670 K. (Zinc melts at 692 K.) Their measurements, made at 10 MHz, demonstrated there is no appreciable frequency dependence of the elastic constants of zinc. Waterman [26] measured four  $C_{ij}$ 's as part of an attenuation study. Garland and Dalven [27] focused on the temperature range 4–77 K using an experimental method resembling that used by Alers and Neighbors. They had access to a cylindrical single crystal 5.5 cm long and 8.1 cm in diameter.

The most recent report of the elastic constants of zinc was by Musgrave [28]. His  $C_{ij}$  values are considerably lower than the best values in table 2; the reason for this is unclear.

Swartz and Elbaum [29] did not report  $C_{ij}$  values, but they measured them during a preliminary study of the third-order elastic constants of zinc, and they reported their  $C_{ij}$ 's agreed within 0.5 percent with those reported by Alers and Neighbors.

Thus, both the  $S_{ij}$ 's and the  $C_{ij}$ 's of zinc are reasonably well known except for  $S_{12}$  (sixty-one percent uncertainty),  $S_{12}$  (seventeen percent uncertainty), and  $C_{13}$  (thirteen percent uncertainty).

## 6. Temperature Variations of Second-Order Single-Crystal Elastic Constants

In a Debye model, which is characterized by a harmonic interatomic potential, elastic constants do not change with temperature. Thus, elastic-constant temperature-dependence is a higher-order effect, related to third-order and fourth-order elastic constants.

Despite considerable study on the problem, elastic-constant/temperature relationships cannot be described simply theoretically. Temperature behavior cannot be predicted a priori, and elastic-constant/temperature anomalies cannot be explained even a posteriori. Interested readers may consult the review by Leibfried and Ludwig [30], which deals in depth with anharmonic effects, and the recent study by Garber and Granato [31,32], which uses a quasiharmonic-anisotropic-continuum model.

Second-order elastic-constant temperature dependencies are usually described by various semi-empirical models. A representative example is due to Varshni [33], and it is based on an Einstein-oscillator model. In this model, elastic constants vary with temperature according to

$$C = C^{\circ} - s/[\exp(t/T) - 1], \quad (15)$$

which contains three adjustable parameters:  $C^{\circ}$  is the elastic constant at zero temperature,  $t$  is the Einstein temperature (electronic effects being absent), and  $-s/t$  is the high-temperature slope  $dC/dT$ . Varshni did not apply this equation to zinc, but he showed it described accurately the  $C_{ij}$  temperature behavior of many materials, including magnesium, which is c.p.h. Materials obeying eq (15), at least approximately, are described herein as regular.  $C_{ij}$ 's with regular temperature behavior show zero slope at zero temperature in accordance with the third law of thermodynamics; monotonically decreasing values with increasing temperature, and a linear slope at high temperatures. For the  $S_{ij}$ 's, regular behavior means the same thing except that the elastic constants increase monotonically with increasing temperature.

$S_{ij}$  temperature dependencies are shown in figures 2–7. These data are taken mainly from Alers and Neighbors [25]. A similar study by Garland and Dalven [27] between 4 and 77 K confirms the Alers and Neighbors' results almost exactly in this temperature range. Wert and Tyndall [24] reported the  $S_{11}$  and  $S_{33}$  temperature dependencies between room temperature and 658 K. The agreement for  $S_{11}$  is good, but the agreement for  $S_{33}$ , which was measured indirectly, is poorer, especially at higher temperatures. Wert and Tyndall also reported a maximum in  $2S_{13} + S_{44}$  at about 475 K that was not observed by Alers and Neighbors. The cause of this discrepancy is unclear. All the  $S_{ij}$ 's except  $S_{12}$  exhibit essentially regular temperature behavior. The reason for this exception is also unclear. As described above,  $S_{12}$  is the only  $S_{ij}$  with an anomalous sign. The temperature variations of the shear constants  $S_{55}$  and  $S_{66}$  are regular.

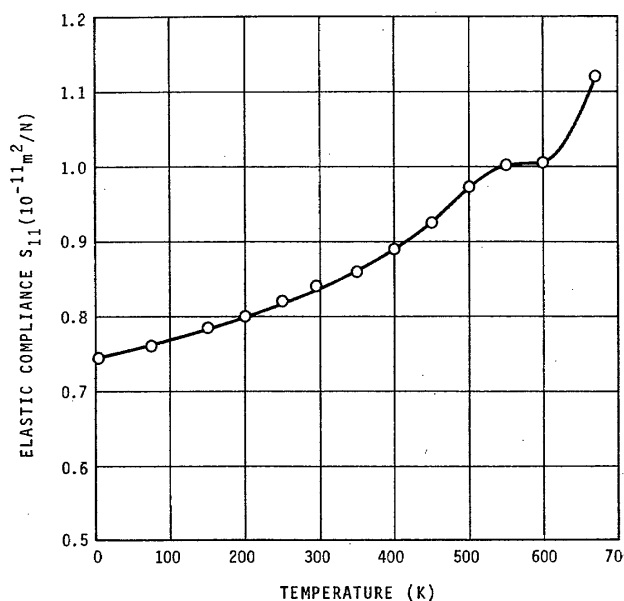


FIGURE 2. Temperature dependence of the elastic compliance  $S_{11} = S_{22}$ .

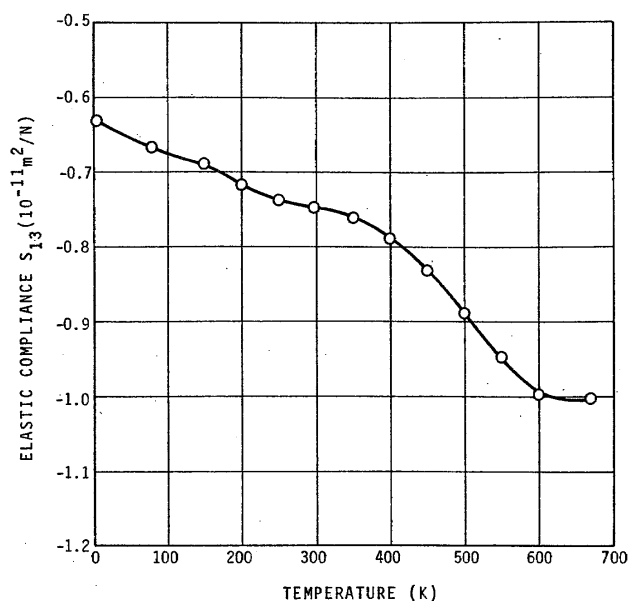


FIGURE 4. Temperature dependence of the elastic compliance  $S_{13} = S_{23}$ .

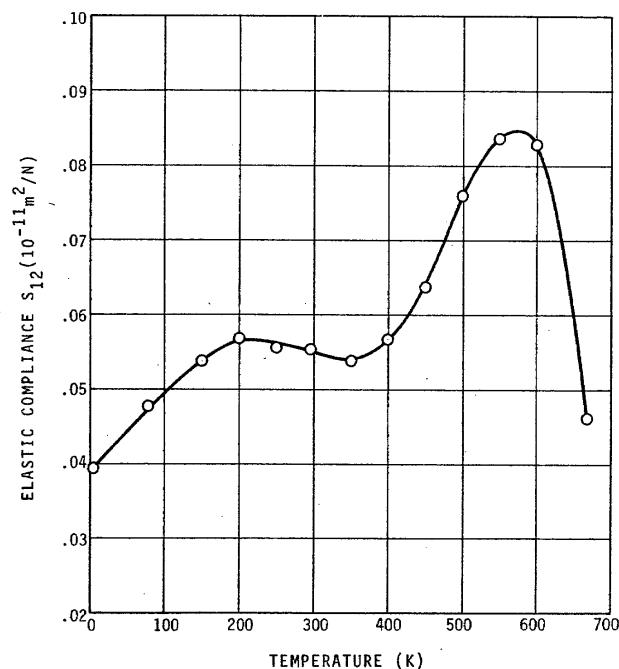


FIGURE 3. Temperature dependence of the elastic compliance  $S_{12}$ .

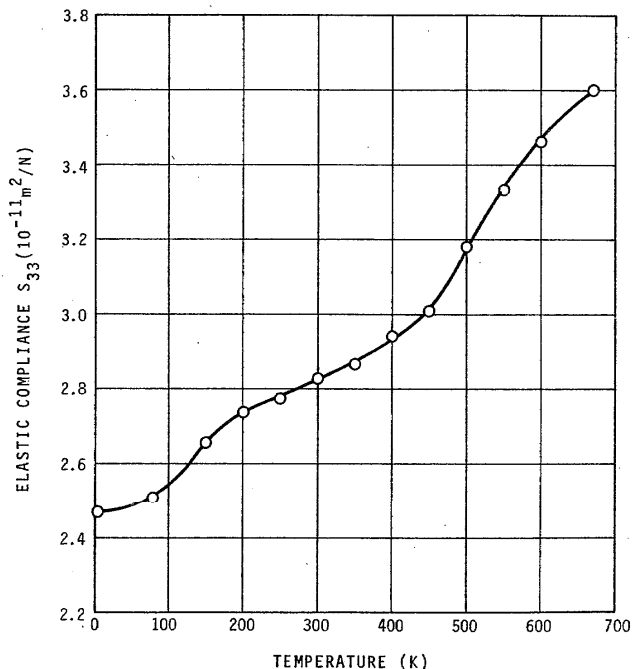


FIGURE 5. Temperature dependence of the elastic compliance  $S_{33}$ .

$C_{ij}$  temperature coefficients are collected in table 3. While only two sets have been reported, their agreement is surprisingly good.

TABLE 3. Temperature coefficients,  $\partial C_{ij}/\partial T$ , of zinc at room temperature in units of  $10^7 \text{ N/m}^2\text{-K}^{-1}$

Source	$C_{11}$	$C_{12}$	$C_{13}$	$C_{33}$	$C_{44}$	$\frac{1}{2}(C_{11}-C_{12})$
Alers, Neighbors [25]	-6.65	0.13		-1.71	-2.82	-3.39
Swartz, Elbaum [29]	-6.61	0.19		-2.02	-2.89	-3.40

Certain useful combinations of the  $S_{ij}$ 's can be formed, and their temperature dependencies are shown in figures 8-11. The linear compressibility perpendicular to the six-fold axis is relatively low and essentially temperature independent. Both linear compressibilities show small irregularities in their temperature dependencies. The bulk compressibility increases smoothly with increasing temperature. The bulk modulus shows similar, but inverse, behavior. All the shear stiffnesses decrease regularly with temperature. Surprisingly,  $C_{44}$ , the shear constant for the basal plane, does not decrease as the melting point is approached. As discussed by Born [34], shear moduli



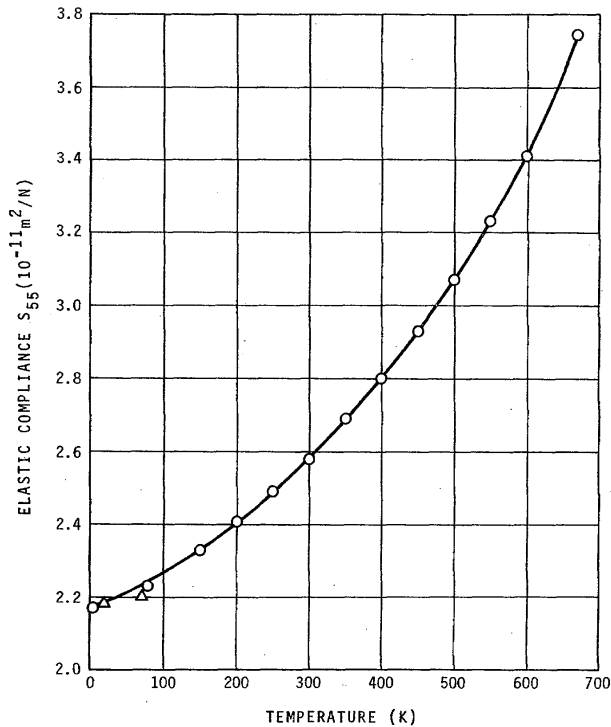


FIGURE 6. Temperature dependence of the elastic compliance  $S_{44} = S_{55}$ .

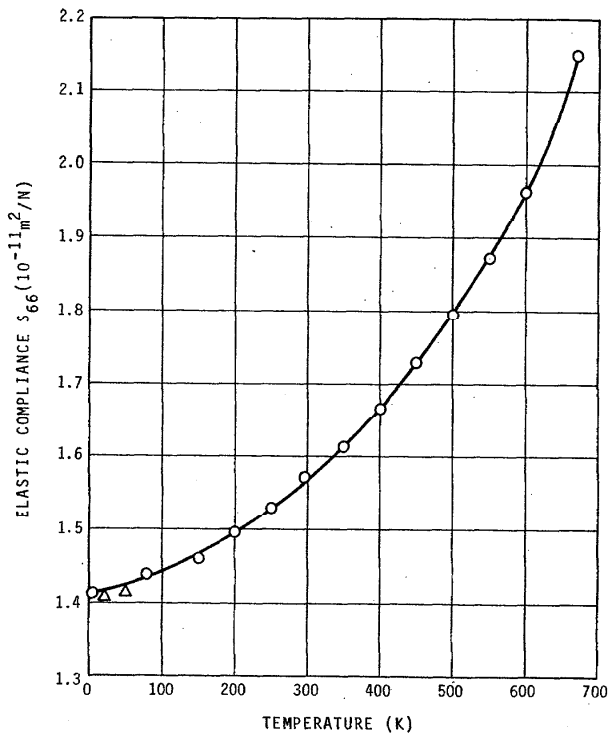


FIGURE 7. Temperature dependence of the elastic compliance  $S_{66} = 2(S_{11} - S_{12})$ .

decreases are often premonitory to melting. Based on the weaker atomic bonds perpendicular to the basal plane, a lattice softening associated with the  $C_{44}$  mode would be expected a priori. In fact, the temperature behaviors of the three shear modes  $C_{44}$ ,  $(C_{11} - C_{12})/2$ , and  $(C_{11} + C_{12} + 2C_{33} - 4C_{13})/6$  are basically the same, showing no anomalous softening before melting.

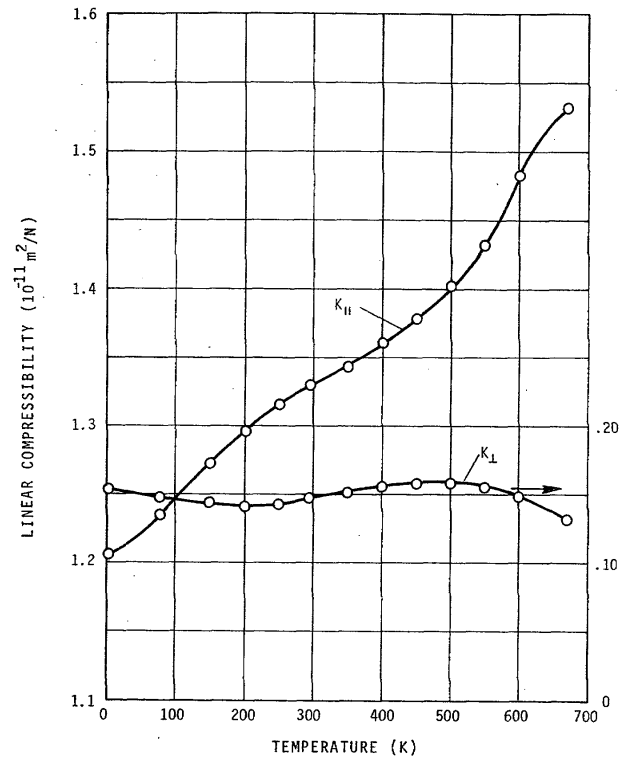


FIGURE 8. Temperature dependencies of the linear compressibilities  $K_{II} = 2S_{13} + S_{33}$  and  $K_I = S_{11} + S_{12} + S_{13}$ .

## 7. Elastic Anisotropy

Zinc is highly anisotropic elastically, and it is important to try to characterize this behavior. Unlike cubic crystals, which have a single anisotropy index, the Zener anisotropy  $2C_{44}/(C_{11} - C_{12})$ , hexagonal crystals have several anisotropy indexes. No generally accepted anisotropy indexes have emerged for hexagonal crystals, and several are considered here. Three were given above in eqs (8–10) in terms of the  $C_{ij}$ 's. However, except for the ratio  $C_{66}/C_{44}$ , none of these correspond to physically simple strains because they involve both shear and dilatational deformations.

There are three independent elastic shear constants for hexagonal crystals; thus, three shear-type anisotropy ratios can be defined: (Values of the  $C_{ij}$ 's are substituted from table 2.)

$$A_1 = \frac{(1/6)(C_{11} + C_{12} + 2C_{33} - 4C_{13})}{C_{44}} = 4.33 \quad (16)$$

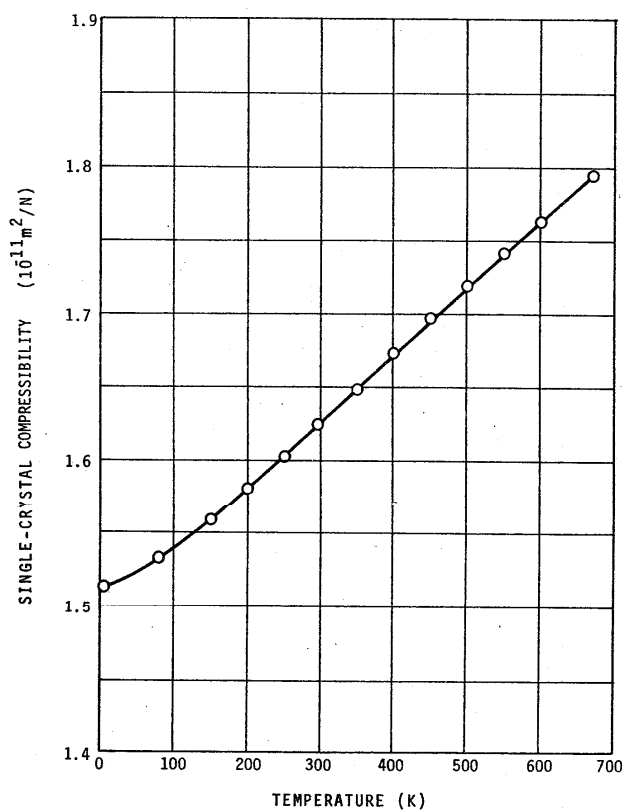


FIGURE 9. Temperature dependence of the single-crystal compressibility  $K = 2(S_{11} + S_{12} + 2S_{13}) + S_{33}$ .

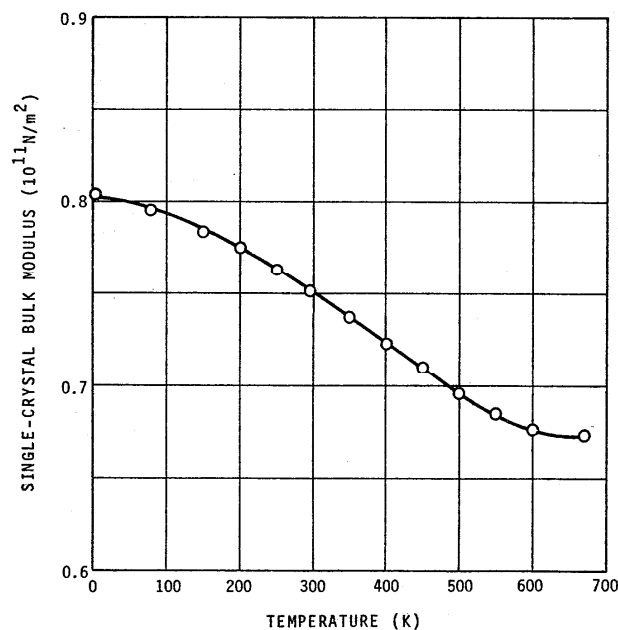


FIGURE 10. Temperature dependence of the single-crystal bulk modulus  $B = 2(C_{11} + C_{12} + 2C_{13}) + C_{33}$ .

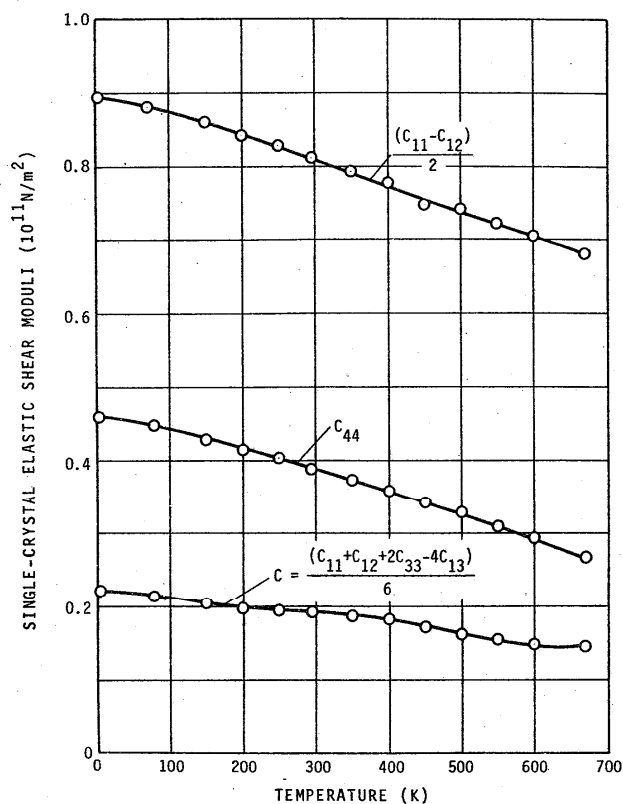


FIGURE 11. Temperature dependencies of three of the single-crystal elastic shear moduli.

$$A_2 = \frac{2C_{44}}{(C_{11} - C_{12})} = 0.61, \quad (17)$$

and

$$A_3 = A_1 A_2 = \frac{(1/3)(C_{11} + C_{12} + 2C_{33} - 4C_{13})}{C_{11} - C_{12}} = 2.64. \quad (18)$$

If zinc were elastically isotropic, all these ratios would be unity.

One useful anisotropy index can be obtained from the  $S_{ij}$ 's:

$$A_4 = \frac{S_{33}}{S_{11}} = 3.36, \quad (19)$$

the Young's-modulus ratio perpendicular and parallel to the six-fold axis. This result for zinc is consistent with the higher atomic-packing density in the basal plane.

It is also useful to have an anisotropy index for a purely dilatational (no shear components) deformation mode. The most obvious index is

$$A_5 = \frac{K_{\parallel}}{K_{\perp}} = \frac{2S_{13} + S_{33}}{S_{11} + S_{12} + S_{13}} = 8.98, \quad (20)$$

the linear-compressibility ratio parallel and perpendicular to the six-fold axis. Again, this tendency, although per-

haps not its magnitude, is expected from the difference in atomic packing parallel and perpendicular to the basal plane.

The high elastic anisotropy of zinc is demonstrated further in figures 12–17, which show the directional dependencies of Young's modulus, torsion modulus, linear compressibilities, and some of the Poisson ratios. These figures were generated from the data in table 2 and the relationships:

$$\frac{1}{E(\theta)} = S_{33}(\theta) = (S_{11} + S_{33} - S)x^2 + (S - 2S_{11})x + S_{11}, \quad (21)$$

$$\frac{1}{G(\theta)} = \frac{1}{2}(S_{44}(\theta) + S_{55}(\theta)) = S_{44} + \left[ (S_{11} - S_{12}) - \frac{1}{2}S_{44} \right] (1 - x) + 2(S_{11} + S_{33} - S)x(1 - x), \quad (22)$$

$$K(\theta) = S_{11} + S_{12} + S_{13} - (S_{11} - S_{33} + S_{12} - S_{13})x, \quad (23)$$

$$\nu_{31}(\theta) = -\frac{S_{13}(\theta)}{S_{33}(\theta)}, \quad (24)$$

$$\nu_{32}(\theta) = -\frac{S_{23}(\theta)}{S_{33}(\theta)}, \quad (25)$$

where  $x = \cos^2\theta$ , (26)

$$S = 2S_{13} + S_{44}, \quad (27)$$

$$S_{13}(\theta) = xS_{13} + (1 - x)S_{12}, \quad (28)$$

$$S_{23}(\theta) = S_{23}(2x^2 - 2x + 1) + x(1 - x)(S_{22} + S_{23} - 4S_{44}), \quad (29)$$

and  $\theta$  is the angle between the axial direction and the  $c$  axis. Because of the complete rotational symmetry about the  $c$  axis, the elastic constants depend on only one angle,  $\theta$ . If zinc were elastically isotropic, all its representation surfaces would be spheres, and figures 12–17 would be circular sections. Figures 12–15 are symmetrical about the  $z$  axis; figures 16 and 17 are not.

Four anisotropy-ratio temperature dependencies are shown in figure 18. Those ratios involving only shear constants— $A_1$ ,  $A_2$ ,  $A_3$ —show slight temperature dependence. Also,  $A_4$ , which describes uniaxial stretching anisotropy, is almost temperature independent. The usual three anisotropy ratios for hexagonal crystals are shown versus temperature in figure 19. Again, no significant departures from usual behavior are shown. It is insignificant whether these ratios decrease or increase with temperature; only the change matters because the reciprocal ratios are equally valid anisotropy indexes.

The temperature dependence of  $A_5$ , shown in figure 20, is interesting. Its temperature dependence is determined mostly by  $K_{\perp}$  since  $K_{\perp}$  is relatively constant over a wide range of temperature. The increase in  $A_5$  is accompanied

by an increase in the  $c/a$  ratio, tending to confirm the above statements concerning atomic-packing-density effects on linear compressibilities. The small temperature dependence of  $K_{\perp}$  is also interesting. It suggests that atomic bonding within the basal plane is basically different from bonding perpendicular to the plane. Wallace [35] suggested that covalent bonds may occur in the basal plane of zinc, but this suggestion has not been developed further.

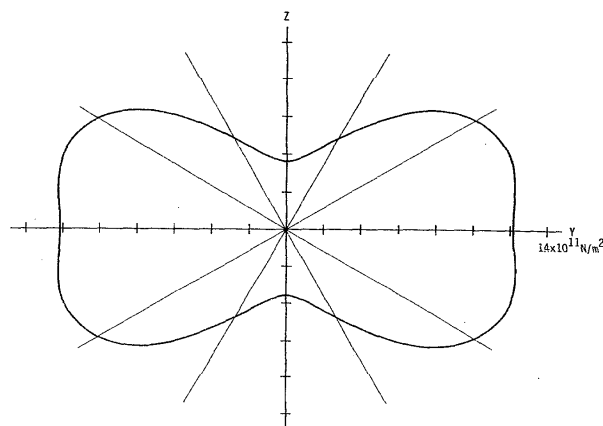


FIGURE 12. Polar plot of Young's modulus, which is symmetrical about the  $z$  axis. This is a central section of the representation surface of the Young's modulus. The length of the radius vector from the origin to the surface is proportional to Young's modulus in that direction. If zinc were elastically isotropic, the surface would be spherical.

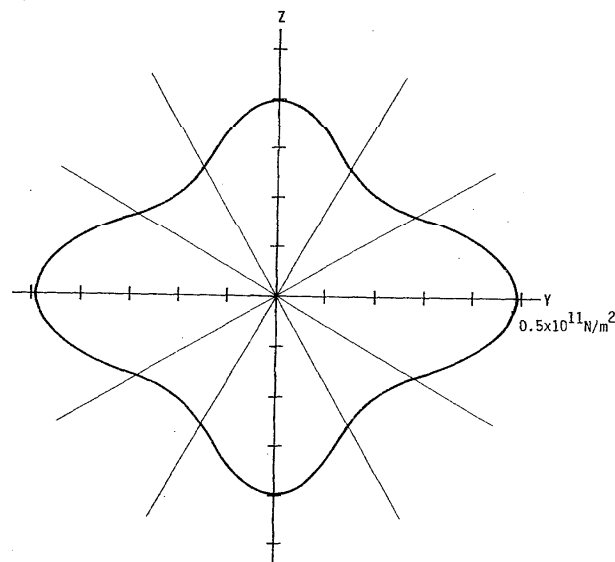


FIGURE 13. Polar plot of the torsional modulus. See figure caption 12.

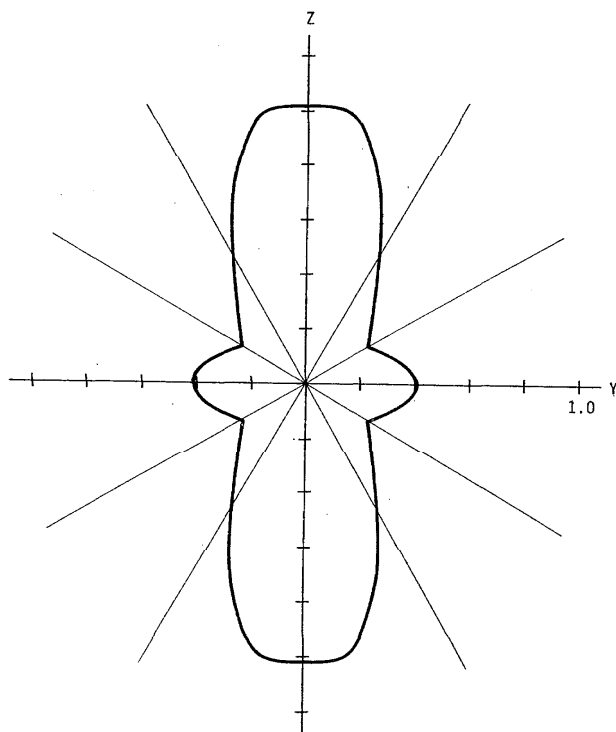


FIGURE 14. Polar plot of the ratio of the shear and Young's moduli. See figure caption 12.

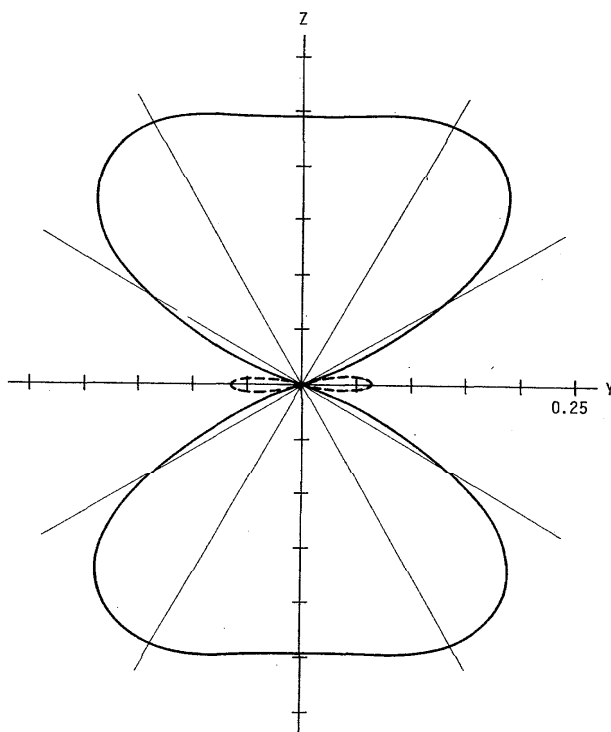


FIGURE 16. Polar plot of the Poisson ratio  $\nu_{31}$ . Dashed curve indicates negative values. Along the  $y$  direction, this is the Poisson ratio  $\nu_{21}$ . This figure is not symmetrical about the  $z$  axis since  $\nu_{13} \neq \nu_{21}$ .

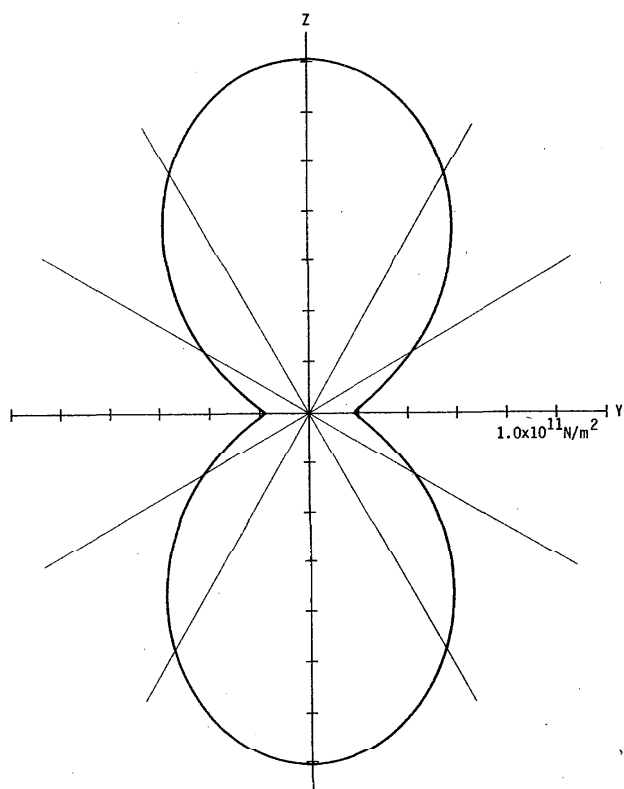


FIGURE 15. Polar plot of the linear compressibility. See figure caption 12.

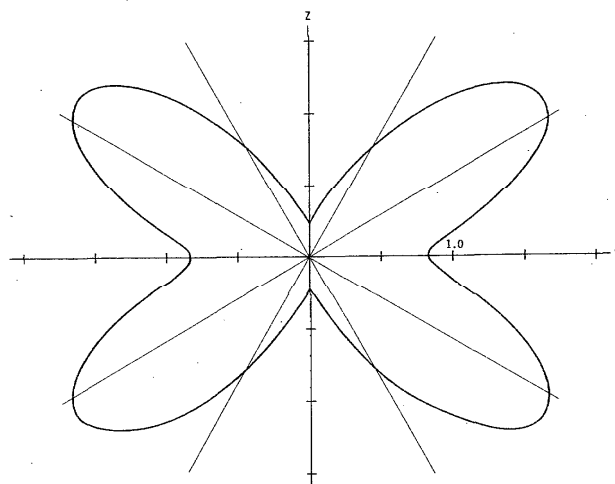


FIGURE 17. Polar plot of Poisson's ratio  $\nu_{32}$ . Along  $y$  direction this is the Poisson ratio  $\nu_{23}$ . This figure is not symmetrical about the  $z$  axis since  $\nu_{12} \neq \nu_{23}$ .

## 8. Elastic Stability

The elastic potential free energy

$$\phi = \frac{1}{2} C_{ij} \epsilon_i \epsilon_j, \quad (30)$$

must be positive-definite,  $\phi = 0$  at the equilibrium, undeformed state and  $\phi > 0$  for any state of mechanical

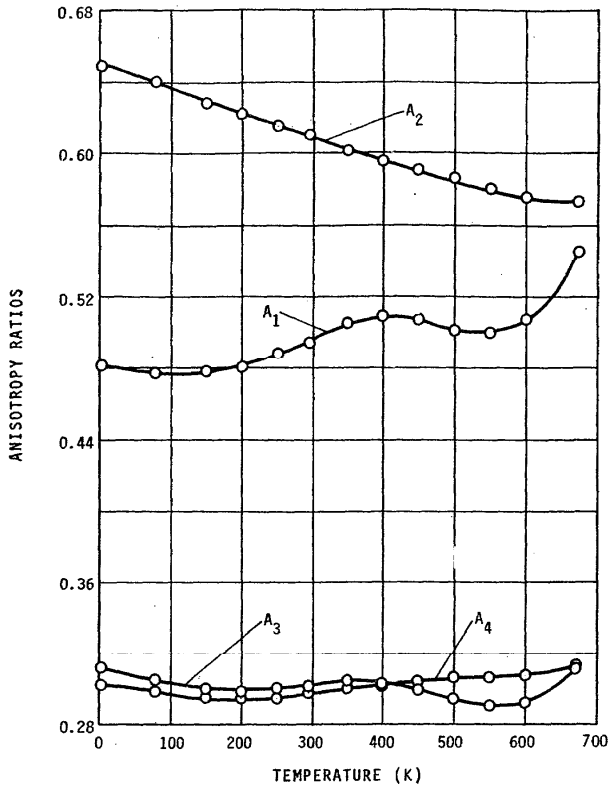


FIGURE 18. Temperature dependencies of four anisotropy ratios defined in text.

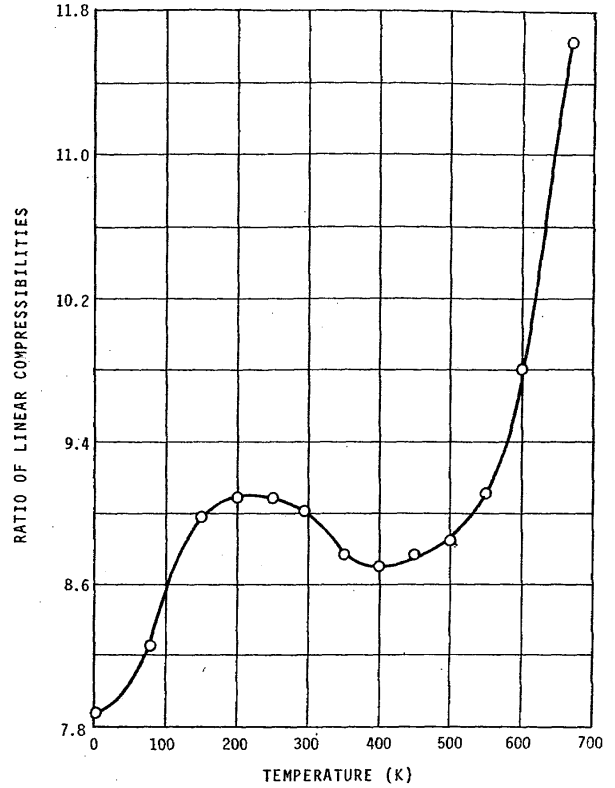


FIGURE 20. Temperature dependence of the ratio of the linear compressibilities  $K_{II}/K_I$ .

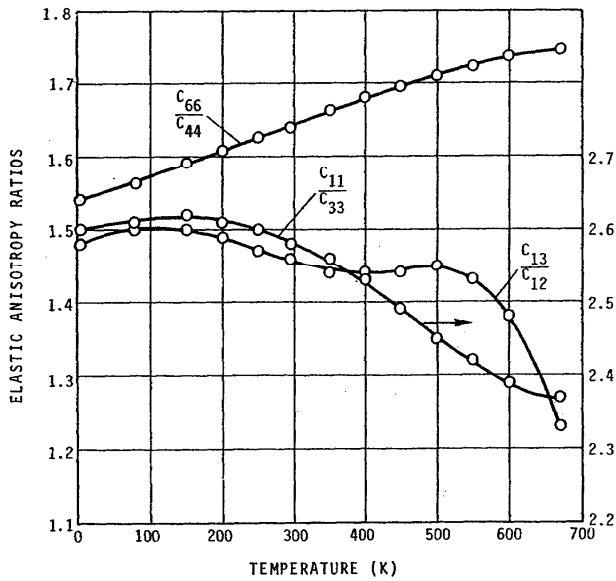


FIGURE 19. Temperature dependencies of three anisotropy ratios that follow from eq (2).

deformation. This requires that the  $C_{ij}$ -matrix principal minors are all positive-definite. From eq (2), there are three independent stability conditions for hexagonal crystals:

$$C_{11} > C_{12}, \tag{31}$$

$$C_{44} > 0, \tag{32}$$

and

$$(C_{11} + C_{12})C_{33} > 2C_{13}^2, \text{ or } C_{11}C_{33} > C_{13}^2. \tag{33}$$

Equations (31 and 32) are identical to the cubic-symmetry stability conditions and eq (33) reduces to  $(C_{11} - C_{12}) > 0$  if  $C_{11}$  and  $C_{12}$  are substituted for  $C_{33}$  and  $C_{13}$ , respectively.

The following stability ratios are obtained for zinc at room temperature from data in table 2:

$$C_{11}/C_{12} = 4.50,$$

$$C_{11}C_{33}/C_{13}^2 = 3.70.$$

Thus, zinc is quite stable with respect to all elastic deformations. It shows no strong tendency to become unstable with increasing temperature or pressure or with small amounts of common alloying elements.

Elastic-stability-criteria temperature dependencies are shown in figure 21. Zinc becomes less stable with increasing temperatures, but it remains stable at temperatures near its melting point. It would be interesting to study carefully the  $C_{11}$ - $C_{12}$  shear mode at temperatures very near the melting point.

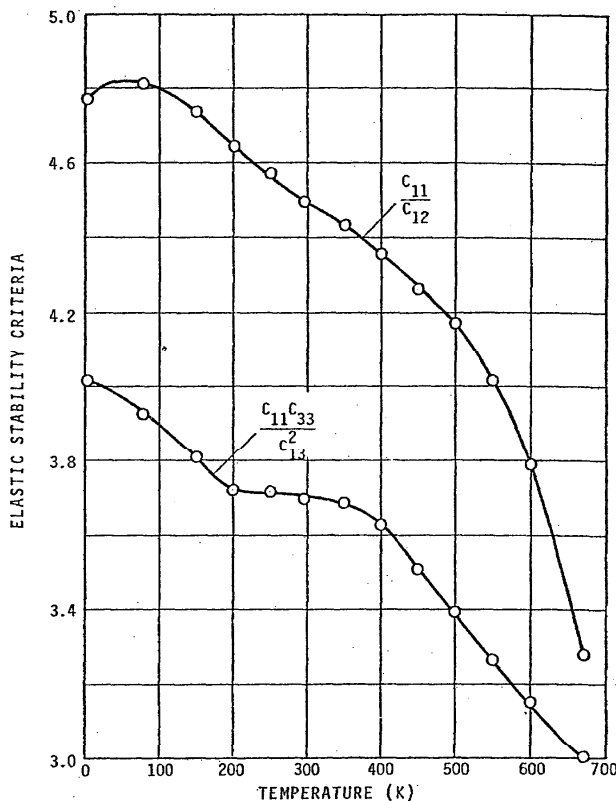


FIGURE 21. Temperature dependencies of the Born and Huang elastic stability criteria.

### 9. Central Forces

If atoms are at centers of symmetry, if interatomic forces are purely central (angular forces are absent), and if the crystal is stress free, then the so-called Cauchy relationships are obtained among the elastic constants. For hexagonal crystals there are two Cauchy relationships for the second-order elastic constants:

$$C_{13} = C_{44}, \quad (34)$$

and

$$C_{11} = 3C_{12}. \quad (35)$$

The first corresponds to the familiar  $C_{12} = C_{44}$  Cauchy relationship for cubic crystals. These relationships are necessary but not sufficient conditions for central interatomic forces existing in crystals. These relationships can be satisfied accidentally in crystals bound by noncentral interatomic forces.

For zinc, as shown by the data in table 2,  $C_{13}/C_{44} = 1.37$  and  $C_{11}/3C_{12} = 1.50$ . Thus, the Cauchy relationships do not hold for zinc. This means either that internal strains break the Cauchy relationships or that the interatomic potential has a strong non-central component. The latter is consistent with the above discussion concerning possible covalent bonds existing within the basal planes; forces localized to a plane are obviously non-central. However, other non-central forces might also have a role in zinc. For example, in hexagonal metals  $C_{13} - C_{44}$  is sometimes interpreted as equal to the electron-gas bulk modulus,  $B_e$ . A free-electron-model calculation for  $B_e$  gives a value considerably larger than  $C_{13} - C_{44}$ . This implies that some valence electrons are not free and that they may contribute to covalent-type bonding.

Deviations from the two Cauchy relationships change considerably with temperature, as shown in figure 22. The relationship involving the shear constant  $C_{44}$  is better satisfied at low temperatures. The relationship between  $C_{11}$  and  $C_{12}$  is better satisfied at high temperatures; extrapolation shows that this relationship is satisfied exactly at the melting temperature.

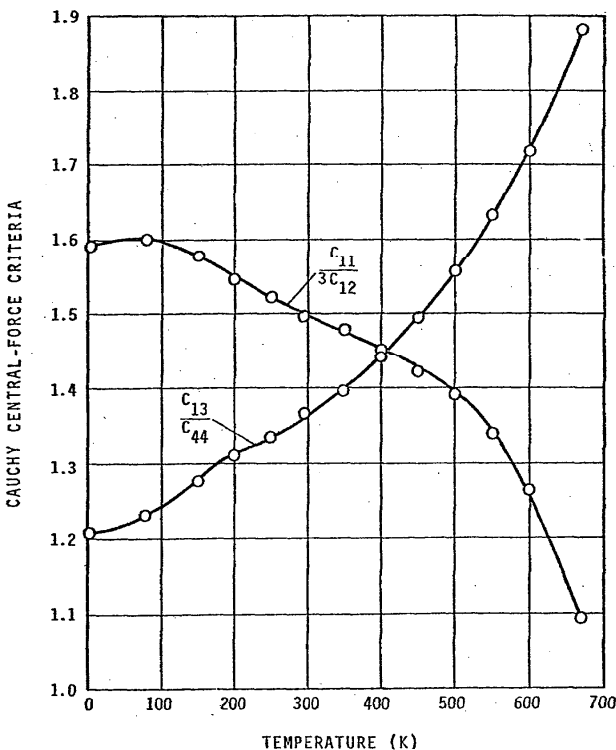


FIGURE 22. Temperature dependencies of the Cauchy central-force criteria.

### 10. Experimental Polycrystalline Elastic Constants

Polycrystalline elastic-constant data are collected in table 4 for  $E$  = Young's modulus,  $G$  = shear modulus,  $B$  = bulk modulus,  $K$  = compressibility, and  $\nu$  = Poisson's ratio. The relative paucity of data is surprising consider-

ing the many practical uses for zinc and its alloys in the form of polycrystalline aggregates. As discussed in the next section, this situation can be remedied by using the single-crystal elastic-constant data.

### 11. Polycrystalline Elastic Constants Computed from Single-Crystal Data

Computing polycrystalline elastic constants from single-crystal elastic constants is part of the more general average-tensor-property problem. Elastic constants are fourth-rank tensors, and their average values were discussed first by Voigt [36] in 1889. As pointed out by Landau and Lifshitz [37], "There is . . . no general relation between the moduli of elasticity of a polycrystal and those of a single crystal of the same substance." Thus, many different, and some very ingenious, approximations to the elastic-constant averaging problem have been suggested. This subject has not been reviewed critically; but Ledbetter [38] discussed eight averaging methods for cubic crystals, a symmetry case where more than twenty averaging methods have been proposed. For cubic symmetry, the averaging problem requires solving for the macroscopic shear modulus,  $G$ , because the second independent macroscopic elastic constant, the bulk modulus,  $B$ , is known unambiguously for cubic crystals.

For hexagonal symmetry, the averaging problem is more complicated because there are uncertainties in averaging for both  $B$  and  $G$ . Using the  $C_{ij}$  data from table 2, results are given in table 5 for five averaging methods. The results are spread considerably, but either Hill's [39] or Percsada's [40] method gives "typical" values when compared with existing polycrystalline data. Thus, either averaging method can be considered to give reasonable results for zinc. All complete  $C_{ij}$  data sets in table 2 were averaged by Hill's method and the results are given in table 6 together with the Voigt and Reuss shear moduli,  $G_V$  and  $G_R$ , which are intermediate calculation results.

The compressibility,  $K$ , in table 6 is simply the reciprocal of  $B$  in the table. The Hill bulk modulus is:

$$B_H = \frac{1}{2}(B_V + B_R), \quad (36)$$

where

$$B_V = \frac{1}{9}(2C_{11} + C_{33} + 2C_{12} + 4C_{13}), \quad (37)$$

and

$$B_R = (2S_{11} + S_{33} + 2S_{12} + 4S_{13})^{-1}. \quad (38)$$

The Hill shear modulus is:

$$G_H = \frac{1}{2}(G_V + G_R), \quad (39)$$

where

$$G_V = \frac{1}{15}(2C_{11} + C_{33} - C_{12} - 2C_{13} + 6C_{44} + 3C_{66}), \quad (40)$$

and

$$G_R^{-1} = \frac{1}{15}(8S_{11} + 4S_{33} - 4S_{12} - 8S_{13} + 6S_{44} + 3S_{66}). \quad (41)$$

Averaged-polycrystalline elastic-constant uncertainties are two to five percent due to  $C_{ij}$  uncertainties and due to propagation of error. This is an important result: given the validity of the averaging method, then polycrystalline elastic constants can be obtained more accurately by aver-

TABLE 4. Experimental elastic constants of polycrystalline zinc.  $E$ ,  $G$ , and  $B$  have units of  $10^{11}$  N/m<sup>2</sup>;  $K$  has units of  $10^{-11}$  m<sup>2</sup>/N;  $\nu$  is dimensionless. Values in parentheses are derived from other data.

Source	$E$	$G$	$B$	$K$	$\nu$	Comments	Method	
Grüneisen [70]	1.206					Cited in Köster [75]	Static	
Richards [71]			0.59	1.7				Static
Adams et al. [72]			0.574	1.74				Static
Bridgman [18, 68]			0.642	1.558				Static
Sieglerschmidt [73]	0.857				0.299	Rolling direction	Static	
	0.991				0.226	Transverse direction	Static	
Bridgman [21]			0.589	1.697		Cited in Köster [75]	Static	
Guillet [74]	0.785							
Bridgman [69]			0.613	1.632		200° C rolling temperature Room-temperature rolled	Dynamic: resonance Dynamic: resonance	
Köster [75]	0.992		(0.478)	(2.090)	(0.150)			
Wegria et al. [41]	1.005	0.437	(0.360)	(2.774)	(0.024)			
	1.030	0.503						
Average values	0.97	0.47	0.60	1.66	0.26			
Standard deviations	0.14	0.05	0.03	0.08	0.05			
Percentage uncertainties	14	10	5	5	20			

aging single-crystal data than by many measurements on polycrystals. One problem always encountered in measuring polycrystalline elastic constants is texture, non-random distribution of orientations of crystallites comprising the aggregate. Textures are an acute problem in zinc because it has high elastic anisotropy. Thus, the polycrystalline elastic constants of zinc are best estimated by the averaged single-crystal elastic constants shown in table 6. The H subscript indicates they were obtained by averaging the single-crystal data using the Hill [39] arithmetic method.

## 12. Temperature Dependence of the Polycrystalline Elastic Constants

Only one report [41] exists on the temperature dependence of the polycrystalline elastic constants of zinc; it is limited to the Young's and shear moduli and to temperatures between room temperature and 575 K. To remedy this data scarcity, the single-crystal-elastic-constant/temperature data described above were converted to polycrystalline values. Peresada's [40] averaging method was used because it is computationally simple, it avoids the

TABLE 5. Practical elastic constants  $E$  = Young's modulus,  $G$  = shear modulus,  $B$  = bulk modulus,  $K$  = compressibility,  $\nu$  = Poisson's ratio obtained by averaging room-temperature single-crystal elastic data by several methods.  $E$ ,  $G$ , and  $B$  have units of  $10^{11}$  N/m<sup>2</sup>;  $K$  has units of  $10^{-11}$  m<sup>2</sup>/N;  $\nu$  is dimensionless. The Peselnick and Meister values are arithmetic averages of their two bounds.

Averaging method	$E$	$G$	$B$	$K$	$\nu$
Voigt [36]	1.121	0.448	0.751	1.332	0.251
Peselnick, Meister [76]	1.026	0.410	0.686	1.459	0.251
Hill [39]	0.993	0.395	0.683	1.464	0.258
Peresada [40]	1.010	0.403	0.680	1.471	0.253
Reuss [77]	0.863	0.341	0.615	1.626	0.266
Average values	1.003	0.399	0.683	1.470	0.256

$C_{ij}$  or  $S_{ij}$  averaging dilemma, and it gives reasonable results. In Peresada's method, the bulk modulus is

TABLE 6. Practical elastic constants  $E$  = Young's modulus,  $G$  = shear modulus,  $B$  = bulk modulus,  $K$  = compressibility and  $\nu$  = Poisson's ratio derived from single-crystal elastic data by Hill's method. Units are  $10^{11}$  N/m<sup>2</sup> for  $E$ ,  $G$ , and  $B$ ;  $10^{-11}$  m<sup>2</sup>/N for  $K$ ; and  $\nu$  is dimensionless.

Source	$E_H$	$G_H$	$B_H$	$K_H$	$\nu_H$	$G_V$	$G_R$
Grüneisen, Goens [16]	0.977	0.395	0.617	1.620	0.236	0.441	0.349
Bridgman [18, 68]	1.018	0.411	0.649	1.542	0.239	0.463	0.358
Goens [19]	1.004	0.403	0.656	1.525	0.245	0.462	0.343
Hanson [20]	(1.092)	(0.435)	(0.752)	(1.330)	0.258	(0.503)	0.366
Hanson [20]	0.971	0.397	0.584	1.713	0.223	0.496	0.369
Tyndall [22]	(1.063)	(0.432)	0.658	1.521	0.231	0.496	0.367
Wert, Tyndall [24]	0.983	0.393	0.656	1.525	0.250	0.447	(0.339)
Alers, Neighbors [25]	0.996	0.396	0.683	1.464	0.257	0.448	0.343
Waterman [26]	1.005	0.405	0.645	1.551	0.240	0.451	0.359
Musgrave [28]	0.965	0.408	(0.506)	(1.974)	(0.182)	0.455	0.360
Average values	0.990	0.401	0.644	1.558	0.242	0.462	0.357
Standard deviations	0.019	0.007	0.030	0.076	0.012	0.020	0.010
Percentage uncertainties	2	2	5	5	5	4	3

$$B_P = (B_V B_R)^{1/2}, \quad (42)$$

where  $B_V$  and  $B_R$  are the Voigt and Reuss bulk moduli described above. The shear modulus is given by equating the determinants of the  $6 \times 6$   $C_{ij}$  matrices for the hexagonal and isotropic cases, and the result is

$$G_P = \left( \frac{C_{44}^2 (C_{11} - C_{12})^2 C}{24B} \right)^{1/5}, \quad (43)$$

where

$$C = (C_{11} + C_{12}) C_{33} - 2C_{13}^2. \quad (44)$$

The Young's modulus and Poisson's ratio are then given by the usual isotropic-media relationships:

$$E = 9GB/(G + 3B), \quad (45)$$

and

$$\nu = E/(2G) - 1. \quad (46)$$

Calculation results for Young's modulus, the shear modulus, and Poisson's ratio are shown in figures 23–25. All three curves show regular behavior. Room-temperature values of the temperature derivatives are given in table 7.

## 13. Sound Velocities

Sound velocities are related intimately to the elastic constants. In fact, sound-velocity measurements provide a convenient and accurate method for determining the elastic constants. Both resonance and pulse techniques yield sound velocities,  $v$ , that are related to the elastic constants,  $C$ , by a general relationship

$$C = \rho v^2, \quad (47)$$

where  $\rho$  is the mass density.



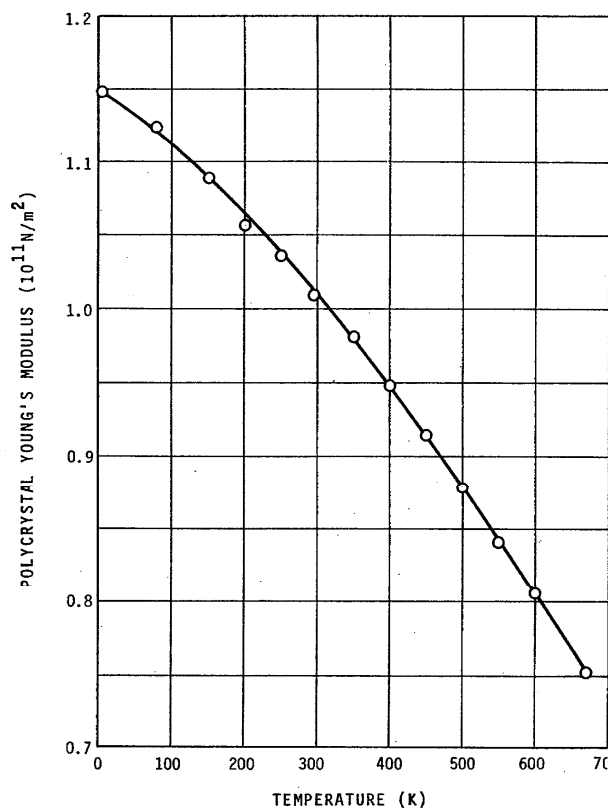


FIGURE 23. Temperature dependence of the polycrystalline Young's modulus computed by averaging single-crystal data.

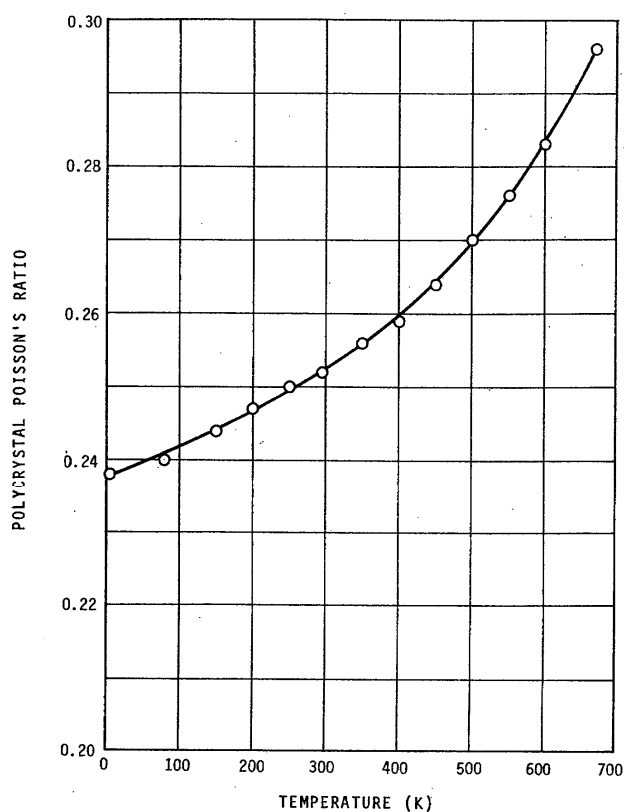


FIGURE 25. Temperature dependence of the polycrystalline Poisson's ratio computed by averaging single-crystal data.

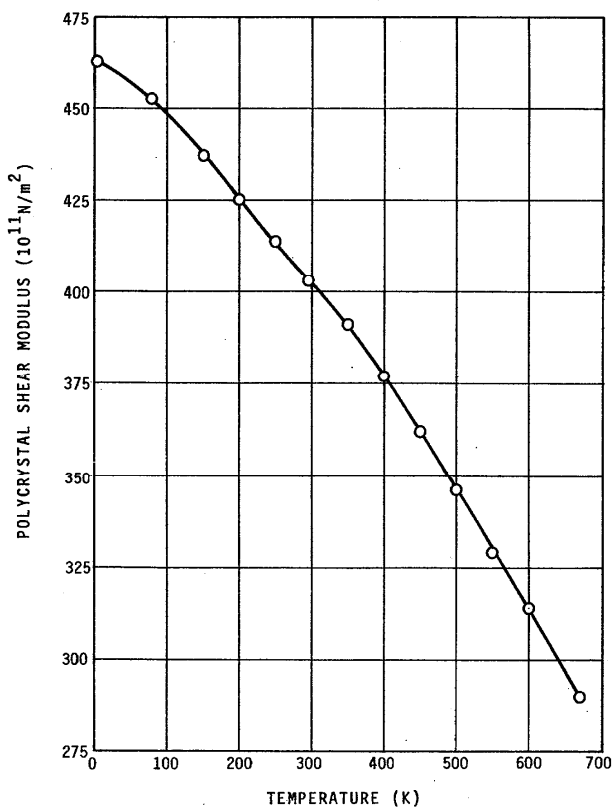


FIGURE 24. Temperature dependence of the polycrystalline shear modulus computed by averaging single-crystal data.

Two kinds of sound waves can be propagated in solids: longitudinal waves and transverse waves, where the particle displacements are parallel and perpendicular, respectively, to the propagation direction. The longitudinal-wave velocity in a quasi-isotropic material is

$$v_l = [(B + \frac{4}{3}G)/\rho]^{1/2}, \quad (48)$$

and the transverse-wave velocity is

$$v_t = (G/\rho)^{1/2}. \quad (49)$$

TABLE 7. Temperature coefficients,  $(1/C)(\partial C/\partial T)$ , of the polycrystalline elastic constants of zinc at room temperature in units of  $10^{-4}/K$ .

Source	$E$	$G$	$B$	$\nu$	$K$
Alers, Neighbors [25]	-5.55	-5.96	-3.16	2.38	2.86

The mean velocity is given by a reciprocal-cube average

$$v_m^{-3} = \frac{1}{3}(v_l^{-3} + 2v_t^{-3}), \quad (50)$$

where there are two transversely polarized waves for each longitudinally polarized wave.

In a single crystal, waves are generally neither purely longitudinal nor purely transverse, but they are mixed modes that are either quasi-longitudinal or quasi-transverse. Wave velocities in single crystals are given by the three  $\rho v^2$  roots of the Christoffel equation

$$\det (C_{ijkl} x_j x_k - \rho v^2 \delta_{il}) = 0, \quad (51)$$

where  $C_{ijkl}$  is the fourth-rank elastic constant tensor,  $x_i$  are unit-wave-vector components relative to the crystal axes, and  $\delta_{il}$  is the Kronecker delta. For each wave vector  $\mathbf{x}$ , there are three distinct real roots  $\rho v^2$  to eq (51). The mean velocity for the single crystal is then

$$3v_m^{-3} = \sum_{\alpha=1,3} v_\alpha^{-3} d\Omega/4\pi, \quad (52)$$

where the  $v_\alpha$ 's are roots of eq (51) and  $d\Omega$  is the solid-angle increment.

Sound velocities in zinc are shown versus temperature in figure 26. All three velocities are well behaved, decreasing smoothly with increasing temperature. Obviously, the mean velocity is determined mainly by the transverse velocity.

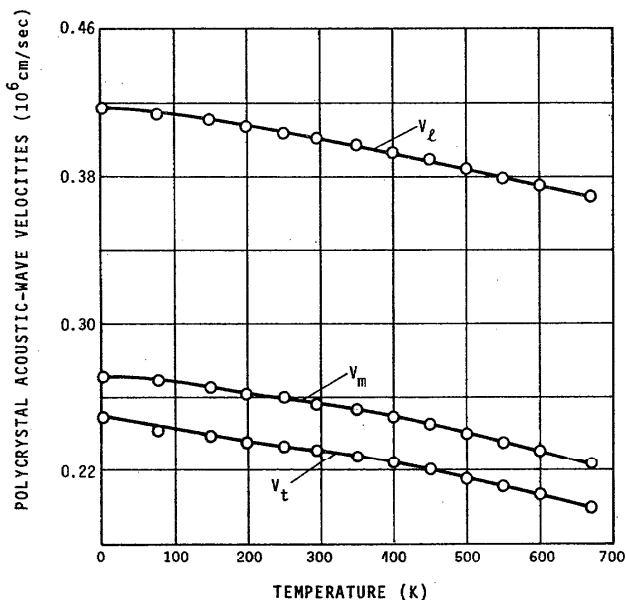


FIGURE 26. Temperature dependencies of the longitudinal, transverse, and mean sound velocities computed from the averaged single-crystal data.

#### 14. Elastic Debye Temperature

The single parameter providing most information about the widest range of solid-state phenomena is the Debye temperature,  $\theta$ , which can be determined by various methods, including: calorimetric, x-ray, electrical resistivity, and elastic. The calorimetric method, which measures specific heat versus temperature at low temperatures and fits the data to a  $(T/\theta)^3$  curve, is the most familiar. At zero temperature, the elastic and the calorimetric Debye temperatures are identical. However, the elastic method for

determining  $\theta$  has several advantages: the experiment is simpler; results are less inaccurate (0.1 percent inaccuracies in wave velocities are achievable); the elastic Debye temperature has a much smaller temperature dependence, especially at low temperatures; the elastic method is more direct; and there are no non-lattice contributions.

The elastic Debye temperature is proportional to the mean elastic wave velocity:

$$\theta = K v_m, \quad (53)$$

where

$$K = \frac{h}{k} \left( \frac{3}{4\pi V_a} \right)^{1/3}, \quad (54)$$

where  $h$  is Planck's constant,  $k$  is Boltzmann's constant, and  $V_a$  is the atomic volume. The mean acoustic-wave velocity is given by eq (50).

The reported Debye temperatures of zinc are given in Table 8. Only elastic and calorimetric values are included because they are more reliable. The data spread is surprisingly wide. Clearly many of these values, both calorimetric and elastic, are incorrect because of the high anisotropy of zinc. In the elastic case, high anisotropy means that the usual approximations for reducing the  $C_{ij}$ 's to  $\theta$  are insufficient and that more exact computational procedures are required. The heat capacity of a highly anisotropic material is also difficult to analyze; it may contain a  $T^5$  term as well as linear and cubic terms. Garland and Silverman [42] discussed this problem, and they concluded that the best calorimetric  $\theta$  value is 322 K and the best elastic  $\theta$  value is 328 K. Because the two values must be identical, because the elastic value is considered more accurate, and because the elastic value has been determined carefully by both Alers and Neighbors [25] and Garland and Dalven [27], the value recommended here is  $\theta = 328$  K.

The Debye- $\theta$  temperature dependence is shown in figure 27. It was computed from Alers and Neighbors' [25]  $C_{ij}$ 's using Peresada's [40] averaging method. Because Peresada's method is only approximate, the calcu-

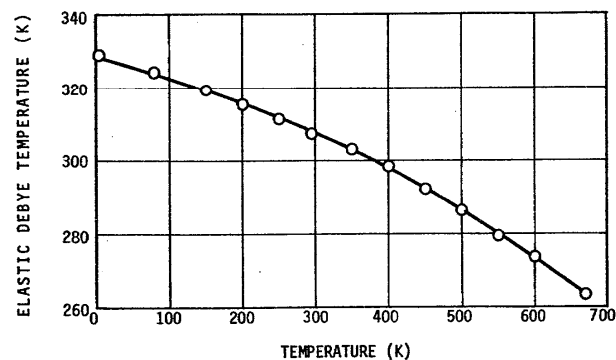


FIGURE 27. Temperature dependence of the elastic Debye temperature computed from averaged single-crystal data and fitted to the recommended zero-temperature value from table 8.

lated curve was fitted to  $\theta = 328$  K at  $T = 0$  K. The temperature dependence calculated by Peresada's method should be quite reliable even though the absolute values differ slightly from exact-calculation results.

TABLE 8. Debye temperature,  $\theta$ , of zinc in kelvins

Source	$\theta$	Comments
Grüneisen, Goens [78]	305	Average elastic-wave velocities
Clusius, Harteck [79]	205	Heat capacity
Keesom, Ende [80]	321	Heat capacity, recalculated by Keesom and Pearlman [87]
Keesom, Haantjes [81]	235	Heat capacity, reported in Holm [98]
Silvidi, Daunt [82]	291	Heat capacity, powders and bulk
Post [83]	231.1	Analysis of Grüneisen, Goens [78] room-temperature data
Blackman [84]	305	Numerical integration, after Grüneisen
Blackman [84]	301	Hopf-Lechner-type calculation, after Honnefelder
Smith [85]	306	Heat capacity
Betts, Bhatia, Horton [86]	303.5	Polynomial expansion of Grüneisen, Goens room-temperature data
Keesom, Pearlman [87]	308	Recommended value in a review paper
Alers, Neighbors [88]	320	Graphical integration
Alers, Neighbors [88]	327.1	Series-expansion method of Betts et al. [86]
Garland, Dalven [27]	327	Numerical integration
Seidel, Keesom [89]	309	Heat capacity
Zavaritskii [90]	340	Temperature-wave method
Wolcott [91]	328.7	Numerical integration of Garland, Dalven [26] data
Srinivasan [92]	319	Heat capacity
Garland, Silverman [42]	322	Analysis of existing heat-capacity data
Zimmerman, Crane [93]	336	Heat capacity, single crystal and polycrystal
Anderson [94, 95]	328.3	Numerical integration of Alers, Neighbors [24] data
Reddy [96]	222	Boas [99] method for average wave velocities
Robie, Edwards [97]	304	Numerical integration of Alers, Neighbors [24] data
Recommended value	328	

### 15. Third-Order Single-Crystal Elastic Constants

Third-order elastic constants reflect the anharmonic forces in crystals. These constants are related to various other anharmonic phenomena: thermal expansion, temperature dependence of second-order elastic constants,

pressure dependence of second-order elastic constants, adiabatic-isothermal elastic-constant differences, temperature variation of the high-temperature specific heat, and lattice-wave interactions. The relationship among different orders of elastic constants is shown by expanding the elastic-deformation free energy,  $\phi$ , in the deformation strains,  $\epsilon_i$ :

$$\phi = \frac{1}{2}C_{ij}\epsilon_i\epsilon_j + \frac{1}{6}C_{ijk}\epsilon_i\epsilon_j\epsilon_k + \frac{1}{24}C_{ijkl}\epsilon_i\epsilon_j\epsilon_k\epsilon_l + \dots \quad (55)$$

where  $C_{ij}$ ,  $C_{ijk}$ , and  $C_{ijkl}$  are the second-order, third-order, and fourth-order elastic constants, respectively. Fourth-order elastic constants have been measured or calculated for some materials, but not yet for zinc.

Zinc was the first hexagonal metal for which a set of third-order elastic constants was determined [29]. Certain linear combinations of the third-order elastic constants of zinc were also determined [43] by studying Hooke's-law deviations in filamentary crystals (whiskers). Discrepancies between these two studies may be related to the impurity method of locking dislocations so that the dislocation strain does not lower the measured elastic constant. Swartz and Elbaum's [29] measurements are supported by the calculations of Srinivasan and Ramji Rao [44], who assumed that anharmonic terms arise only from the central part of the two-body interaction between first, second, and third neighbors. The input for their twelve-parameter model was the second-order elastic constants and data from dispersion relations. The third-order elastic constants of zinc are collected in table 9. These constants are approximately an order of magnitude larger than the second-order constants and they are negative.

### 16. Pressure Derivatives

The five hydrostatic pressure derivatives of the elastic constants of hexagonal crystals are related to the ten third-order elastic constants, and they are often determined separately because a hydrostatic experiment is simpler than a uniaxial-stress experiment. Since third-order elastic constants are related to the third derivative of the interatomic potential with respect to strain, pressure derivatives can give further information concerning the interatomic potential. Also, they have practical applications in high-pressure applications where precisely known elastic constants are important.

Reported hydrostatic pressure derivatives of the elastic constants of zinc are given in table 10. Agreement between experimental and theoretical results is quite impressive

TABLE 9. Third-order single-crystal elastic-stiffness coefficients in units of  $10^{11}$  N/m<sup>2</sup>

Source	$C_{111}$	$C_{112}$	$C_{113}$	$C_{123}$	$C_{133}$	$C_{344}$	$C_{333}$	$C_{222}$	$C_{144}$	$C_{155}$	Comments
Swartz, Elbaum [29]	-17.6	-4.4	-2.7	-2.1	-3.5	-4.4	-7.2	-24.1	-0.1	+2.5	Experimental
Srinivasan, Ramji Rao [44]	-21.9	-6.5	-5.3	0.1	-7.8	-7.8	-25.9	-24.4	-1.1	-4.9	Theoretical, based on $C_{ij}$ 's and dispersion relations

considering the generally anomalous elastic behavior of zinc. Any lattice model of zinc should be able to predict these results before it can be considered seriously for general applications. To date, no studies on the temperature dependencies of the pressure derivatives have been reported.

## 17. Theoretical Studies

A priori predictions of the elastic constants of zinc have proven quite poor. Reasons for this failure of theory include: a relatively complicated crystal structure; two ions per unit cell introduce internal-strain possibilities; a non-ideal  $c/a$  ratio; a relatively high atomic number; and  $d$ -band/conduction-band hybridization. Accounting for these factors makes calculations more difficult and extends usual models beyond their useful limits.

Nevertheless, it is valuable to review the calculations and their implications because an intimate, often synergistic, relationship exists between theory and experiment in solid-state elasticity. First, central-force calculations are reviewed; then more sophisticated models, such as the pseudopotential, are considered briefly.

Expressions for the elastic constants of a hexagonal lattice bound by central forces were given by Hayes [45], extending the approach of Born [34] for cubic lattices. These expressions can be used to calculate the  $C_{ij}$ 's from any central-force interatomic potential—Lennard-Jones, Mie-Grüneisen, Born-Mayer, Morse, Rydberg, Coulomb, etc. But these expressions apply only to lattices with ideal  $c/a$  ratios.

TABLE 10. Pressure derivatives,  $\partial C_{ij}/\partial P$

Source	$C_{11}$	$C_{33}$	$C_{44}$	$C_{66}$	$C_{12}$	$C_{13}$
Swartz, Elbaum [29]	7.52	7.32	4.02	1.48		
Srinivasan, Ramji Rao [44]	7.70	6.50	3.94	2.10	3.51	4.72

A rather complete central-force calculation of the elastic constants of zinc was reported by Rose and Ramsey [46]. From both Morse and Rydberg potential functions, they calculated second-order and third-order elastic constants. The calculation was successful for magnesium, which has a nearly ideal  $c/a$  ratio, but it failed for zinc. In fact, a negative value of  $C_{44}$  was predicted. Based on the Born and Huang [47] stability criteria,  $C_{44}$  is always positive in a mechanically stable lattice.

Assuming a screened-Coulomb potential function, Czachor and Pindor [48] calculated the second-order elastic constants of zinc. This model also gives a negative  $C_{44}$ . The authors concluded that "ion-ion interactions of the proposed type either do not appear or play a rather unimportant role." An alternative view is that this model is simply incomplete.

Some useful expressions for contributions to first-order,

second-order, and third-order elastic constants were derived by Cousins [49] for hexagonal metals with arbitrary axial ratios.

Expressions for hexagonal elastic constants that include both non-ideal  $c/a$  ratios and non-central, arbitrary volume-dependent energies were given by Johnson [50]; his example potentials were limited to central forces.

Bulk moduli of simple metals were discussed by Jones [51] in terms of three energies: ionic-repulsion, electrostatic, and Fermi. Because of the large ratio of the atomic-sphere diameter to the ionic-sphere diameter in zinc, the ionic-repulsion-energy contribution to the elastic constants is expected to be relatively small. If the electrostatic term is also small, and Jones justifies this, then the bulk modulus is determined by the Fermi energy alone. Jones showed that the Fermi-energy contribution to the bulk modulus is

$$B_f = \frac{1}{9} \frac{r^2}{V_0} \left( \frac{\partial^2 E_f}{\partial r^2} \right)_{r=r_0}, \quad (56)$$

where  $V_0$  is the atomic volume,  $E_f$  is the Fermi energy, and  $r$  is the interatomic distance. For zinc,  $B_f = 8.03 \times 10^{11}$  N/m<sup>2</sup>, which exceeds the observed value of 6.06. Jones interpreted this to mean that  $E_0$ , the energy of the lowest state in the conduction band, contributes to the bulk modulus of zinc and that it has a minimum at  $r$  sufficiently less than  $r_0$  so that  $(\partial^2 E/\partial r^2)_{r=r_0}$  is negative.

The first model-pseudopotential calculation of the elastic constants of zinc was reported by Cousins [52], who considered the three shear constants  $C_{44}$ ,  $\frac{1}{2}(C_{11} - C_{12})$ , and  $\frac{1}{6}(C_{11} + C_{12} + 2C_{33} - 4C_{13})$ . Cousins' results were very poor, but he believed they could be improved by modifying the energy-wavenumber relationship. Cousins did not find a negative  $C_{44}$ , but one far too small. Thus, theoretical calculations of the elastic constants of zinc have failed.

Successful lattice dynamics calculations were done for both beryllium ( $c/a = 1.57$ ) and magnesium ( $c/a = 1.63$ ) by King and Cutler [53, 54]. However, no similar calculations have been reported for hexagonal metals where  $c/a$  exceeds ideal. Their calculations are of the first-principles pseudopotential type where the input information consists of: free-ion eigenfunctions and eigenenergies; unit-cell dimensions; atomic number; and valence.

No theoretical values of the elastic constants of zinc are reported in this review because they are too uncertain relative to the experimental values. Considerable theoretical study is in progress, and significant results may emerge soon. In particular, one anticipates that pseudopotential calculations for zinc have not yet matured. In other systems, these calculations have proven useful in elucidating various problems relevant to zinc, including: relative phase stability, axial ratio, defect properties, alloying effects, pressure-volume relationships, lattice dynamics, thermodynamic properties, and elastic constants.

## 18. Miscellaneous Topics

Many studies have been reported that relate closely to the elastic properties of zinc. These studies are of two types: those that contribute further understanding of elastic properties and those that use the elastic constants to deduce non-elastic properties.

In lattice dynamics, the elastic constants are related to the dispersion-curve slopes at infinite wavelength. Several theoretical lattice-dynamics studies on zinc have been reported [44, 55–60]. And some experimental lattice-dynamics studies on zinc have been reported [61–62].

The plastic properties of zinc, such as resistance to plastic deformation, fracture strength, and malleability, were related to the elastic properties by Pugh [63].

The elastic-constant combinations of zinc that are relevant to x-ray diffraction studies have been derived by Evenschor and co-workers [64–65].

Elastic-anisotropy effects on dislocation properties in zinc have been considered by Fisher and Alfred [66].

The problems of root-mean-square atomic displacements and x-ray Debye temperatures in zinc were considered by Skelton and Katz [67].

## 19. Conclusions and Recommendations for Further Studies

In the single-crystal elastic-constant case:

(1) Room-temperature values are well defined experimentally. Further studies here should focus on  $S_{12}$ ,  $C_{12}$ , and  $C_{13}$ .

(2) Based on the careful studies of Alers and Neighbors [25] and Garland and Dalven [27], low-temperature values are also well defined experimentally.

(3) A third high-temperature experiment would be useful to resolve small discrepancies between the Alers and Neighbors [25] study and the Wert and Tyndall [24] study. Whether  $2S_{13} + S_{44}$  has a maximum or increases continuously with temperature is uncertain.

(4) Also, it would be valuable to verify the abrupt decrease in  $S_{12}$  near the melting point since changes of elastic constants near phase transitions are important from the viewpoints of lattice instabilities and soft vibrational modes. Elastic-constant measurements very close to the melting point might elucidate the problem of the bonding of zinc.

(5) Third-order elastic constants are reasonably well defined, but it would be interesting to know their temperature dependencies so that zero-temperature values would be available as checks on theoretical models of the elastic constants of zinc.

(6) The theoretical situation for zinc is dismal. Better theoretical models are required for predicting and correlating the elastic properties. Improved pseudopotential calculations seem appropriate here.

(7) Despite the poor theoretical situation, experimental studies on zinc-alloy single crystals are appropriate.

(8) Effects of well-defined plastic deformations on the

elastic constants of zinc would be very interesting. Dislocation behavior in zinc seems to be relatively well understood; thus, effects of dislocations on the elastic constants could be assessed.

In the polycrystalline elastic-constant case:

(9) The problem of the polycrystalline elastic constants of zinc is ripe for experimental study, particularly at low temperatures. For example, not one ultrasonic-pulse experiment on polycrystalline zinc has been reported. Resonance experiments are less effective here because they measure only  $E$  and  $G$  accurately and both  $B$  and  $\nu$  are also of considerable interest.

(10) Effects of alloying and mechanical deformation have not been studied to any extent.

(11) The problem of averaging—converting single-crystal elastic constants to polycrystalline elastic constants—should be pursued vigorously for hexagonal metals.

(12) As shown by the data in table 8, the Debye-temperature problem needs a careful review, comparing calorimetric and elastic data and distinguishing carefully the many numerical methods in the elastic case.

## Acknowledgment

This study was supported by the NBS Office of Standard Reference Data. Dr. E. R. Naimon of Rockwell International (Rocky Flats) contributed a critical reading of the manuscript.

## 20. References

- [1] Ledbetter, H. M., and Reed, R. P., Elastic properties of metals and alloys. I. Iron, nickel, and iron-nickel alloys, *J. Phys. Chem. Ref. Data* **2**, 531–618 (1973).
- [2] Ledbetter, H. M., and Naimon, E. R., Elastic properties of metals and alloys. II. Copper, *J. Phys. Chem. Ref. Data* **3**, 897–935 (1974).
- [3] Horvick, E. W., Zinc, *Machine Design* **42** (No. 4), 77–79 (1970).
- [4] Hearmon, R. F. S., The elastic constants of anisotropic materials, *Rev. Mod. Phys.* **18**, 409–440 (1946).
- [5] Hearmon, R. F. S., The elastic constants of non-piezoelectric crystals, in *Numerical Data and Functional Relationships in Science and Technology, Group III, Vol. I*, K. H. Hellwege and A. M. Hellwege, eds., Springer-Verlag, Berlin (1969).
- [6] Harrison, W. A., Electronic structure and the properties of metals. II. Application to zinc, *Phys. Rev.* **129**, 519–527 (1963).
- [7] Kaufman, L. and Bernstein, H., *Computer Calculation of Phase Diagrams*, Academic, New York (1970).
- [8] Weaire, D., The structure of the divalent simple metals, *J. Phys. C* **1**, 210–221 (1968).
- [9] Hume-Rothery, W., *Atomic Theory for Students of Metallurgy*, Institute of Metals, London (1948).
- [10] Dehlinger, U., *Theoretische Metallkunde*, Springer-Verlag, Berlin (1955).
- [11] Nye, J. F., *Physical Properties of Crystals*, Oxford U.P., London (1957).
- [12] Fedorov, F. I., *Theory of Elastic Waves in Crystals*, Plenum, New York (1968).

- [13] Musgrave, M. J. P., *Crystal Acoustics*, Holden-Day, San Francisco (1970).
- [14] Lifshitz, I. M., and Rozentsveig, L. N., *Zh. Eksp. Teor. Fiz.* **16**, 967-980 (1946).
- [15] Pynn, R., The O K Debye temperature of hexagonal close-packed metals, *Can. J. Phys.* **49**, 1690-1692 (1971).
- [16] Grüneisen, E., and Goens, E., Untersuchungen an Metallkristallen. I. Elastische Konstanten von Zink und Cadmium, *Z. Phys.* **26**, 235-49 (1924).
- [17] Voigt, W., *Lehrbuch der Kristallphysik*, Teubner, Berlin (1928).
- [18] Bridgman, P. W., Certain physical properties of single crystals of tungsten, antimony, bismuth, tellurium, cadmium, zinc, and tin, *Proc. Am. Acad. Arts Sci.* **60**, 305-383 (1925).
- [19] Goens, E., Über eine verbesserte Apparatur zur statischen Bestimmung des Drillingsmoduls von Kristallstäben und ihre Anwendung auf Zink-Einkristalle, *Ann. Phys.* **16**, 193-809 (1933).
- [20] Hanson, A. W., Elastic behavior and elastic constants of zinc single crystals, *Phys. Rev.* **45**, 324-331 (1934).
- [21] Bridgman, P. W., On the effect of slight impurities on the elastic constants, particularly the compressibility of zinc, *Phys. Rev.* **47**, 393-397 (1935).
- [22] Tyndall, E. P. T., Note on the probable value of the elastic constants of the zinc crystal, *Phys. Rev.* **47**, 398-399 (1935).
- [23] Read, T. A., The internal friction of single metal crystals, *Phys. Rev.* **58**, 371-801 (1940).
- [24] Wert, C. A., and Tyndall, E. P. T., Elasticity of zinc crystals, *J. Appl. Phys.* **20**, 587-589 (1949).
- [25] Alers, G. A., and Neighbors, J. R., The elastic constants of zinc between 4.2 and 670 K, *J. Phys. Chem. Solids* **7**, 58-64 (1958).
- [26] Waterman, P. C., Orientation dependence of ultrasonic attenuation in zinc, *J. Appl. Phys.* **19**, 1190-1195 (1958).
- [27] Garland, C. W., and Dalven, R., Elastic constants of zinc from 4.2 K to 77.6 K, *Phys. Rev.* **111**, 1232-1234 (1951).
- [28] Musgrave, M. J. P., Calculations relating to the propagation of elastic waves in anisotropic media, NPL Basic Physics Division Report No. 7 (1961). Cited in Ref. 101.
- [29] Swartz, K. D., and Elbaum, C., Third-order elastic constants of zinc, *Phys. Rev. B* **1**, 1512-1517 (1970).
- [30] Leibfried, G., and Ludwig, W., Theory of anharmonic effects in crystals, in *Solid State Physics, Vol. 12*, F. Seitz and D. Turnbull, ed., Academic, New York (1961).
- [31] Garber, J. A., and Granato, A. V., Theory of the temperature dependence of second-order elastic constants in cubic materials, *Phys. Rev.* **11**, 3990-3997 (1975).
- [32] Carber, J. A., and Granato, A. V., Fourth-order elastic constants and the temperature dependence of second-order elastic constants in cubic materials, *Phys. Rev.* **11**, 3998-4007 (1975).
- [33] Varshni, Y. P., Temperature dependence of the elastic constants, *Phys. Rev. B* **2**, 3952-3958 (1970).
- [34] Born, M., On the stability of crystal lattices. I, *Proc. Camb. Phil. Soc.* **36**, 160-172 (1940).
- [35] Wallace, W. E., Bonding in the zinc family metals, *J. Chem. Phys.* **23**, 2281-2294 (1955).
- [36] Voigt, W., Ueber die Beziehung zwischen den beiden Elastizitäts-constanten isotroper Körper, *Ann. Physik* **38**, 573-587 (1889).
- [37] Landau, L. D., and Lifshitz, E. M., *Theory of Elasticity*, Pergamon, London (1959), p. 40.
- [38] Ledbetter, H. M., Estimation of Debye temperatures by averaging elastic coefficients, *J. Appl. Phys.* **44**, 1451-1454 (1973).
- [39] Hill, R., The elastic behavior of a crystalline aggregate, *Proc. Phys. Soc. Lond.* **A65**, 349-354 (1952).
- [40] Peresada, G. I., On the calculation of elastic moduli of polycrystalline systems from single crystal data, *Phys. Status Solidi (a)* **4**, K23-K27 (1971).
- [41] Wegria, J., Gouzou, J., and Habraken, L., Variations in the elastic moduli of pure zinc and zinc alloys in relation to temperature, *C.R.M.* **31**, 47-56 (1972).
- [42] Garland, C. W., and Silverman, J., Analysis of specific heat data for zinc, resolution of the calorimetric and elastic  $\theta$  discrepancy, *J. Chem. Phys.* **34**, 781-782 (1961).
- [43] Powell, B. E., and Skove, M. J., Combinations of third-order elastic constants of zinc and cadmium, *J. Appl. Phys.* **4**, 666-667 (1973).
- [44] Srinivasan, R., and Ramji Rao, R., Anharmonic properties of the hexagonal metals, magnesium, zinc and beryllium. I. Lattice dynamics and third order elastic constants, *J. Phys. Chem. Solids* **32**, 1769-1788 (1971).
- [45] Hayes, E. F., Elastic constants for a h.c.p. structure bound by central forces, *Phil. Mag.* **14**, 415-419 (1966).
- [46] Rose, M. F., and Ramsey, R. T., Higher order elastic constants in h.c.p. crystals, *Phys. Status Solidi* **25**, 103-108 (1968).
- [47] Born, M. and Huang, K., *Dynamical Theory of Crystal Lattices*, Oxford U.P., London (1954).
- [48] Czachor, A., and Pindor, A., Dependence of calculated elastic constants on the c/a ratio of hexagonal close-packed metals, *Phys. Status Solidi* **20**, K17-K20 (1967).
- [49] Cousins, C. S. G., Contributions to the first-, second- and third-order elastic shear constants of hexagonal metals for arbitrary axial ratio, *J. Phys. C* **1**, 478-485 (1968).
- [50] Johnson, R. A., Relationship between two-body interatomic potentials in a lattice model and elastic constants, *Phys. Rev. B* **6**, 2094-2100 (1972).
- [51] Jones, H., Structural and elastic properties of metals, *Physica* **15**, 13-22 (1949).
- [52] Cousins, C. S. G., The calculation of the elastic shear constants of hexagonal metals using the optimized model potential, *J. Phys. C* **3**, 1677-1692 (1970).
- [53] King, W. F., and Cutler, P. H., Lattice dynamics of beryllium from a first-principles nonlocal pseudopotential approach, *Phys. Rev. B* **2**, 1733-1742 (1970).
- [54] King, W. F., and Cutler, P. H., Lattice dynamics of magnesium from a first-principles nonlocal pseudopotential approach, *Phys. Rev. B* **3**, 2485-2496 (1971).
- [55] Slutsky, L. J., and Garland, C. C. W., Lattice dynamics of hexagonal close-packed metals, *J. Chem. Phys.* **26**, 787-793 (1957).
- [56] Young, J. A., and Koppel, J. V., Lattice vibrational spectra of beryllium, magnesium, and zinc, *Phys. Rev.* **134**, A1476-A1479 (1964).
- [57] DeWames, R. E., Wolfram, T., and Lehman, G. W., Lattice dynamics, heat capacities, and Debye-Waller factors for Be and Zn using a modified axially symmetric model, *Phys. Rev.* **138**, A717-A728 (1965).
- [58] Gupta, R. P., and Dayal, B., Lattice dynamics of zinc, *Phys. Status Solidi* **13**, 519-527 (1966).
- [59] Brovman, E. G., Kagan, Yu., and Kholas, A., Theory of the vibrational spectra of hexagonal metals, *Soviet Phys.—Solid State* **11**, 733-740 (1969).
- [60] Trott, A. J., and Heald, P. T., The lattice dynamics of the hexagonal close-packed metals, *Phys. Status Solidi (b)* **46**, 361-363 (1971).
- [61] Marliskewski, E., Cold neutron measurement of the phonon dispersion-relation for a zinc single-crystal, *Phys. Lett.* **1**, 338-339 (1962).
- [62] Borgonovi, G., Caglioti, G., and Antal, J. J., A study of the crystal dynamics of zinc, *Phys. Rev.* **132**, 683-688 (1963).

- [63] Pugh, S. F., Relations between the elastic moduli and the plastic properties of polycrystalline pure metals, *Phil. Mag.* **45**, 823-843 (1954).
- [64] Evenschor, P. D., Frohlich, W., and Hauk, V., Calculation of x-ray elastic constants from single crystal coefficients of hexagonally crystallizing metals, *Z. Metallk.* **62**, 38-42 (1972). (In German.)
- [65] Evenschor, P. D., and Hauk, V., Calculation of x-ray elastic constants from single crystal coefficients of hexagonally crystallizing metals, *Z. Metallk.* **63**, 798-801 (1972). (In German.)
- [66] Fisher, E. S., and Alfred, L. C. R., Effects of elastic anisotropy on dislocations in hcp metals, *Trans. Met. Soc. AIME* **242**, 1575-1586 (1968).
- [67] Skelton, E. L., and Katz, J. L., Examination of the thermal variation of the mean square atomic displacements in zinc and evaluation of the associated Debye temperature, *Phys. Rev.* **171**, 801-808 (1968).
- [68] Bridgman, P. W., Some properties of single metal crystals, *Proc. Nat. Acad., Sci.* **10**, 411-415 (1924).
- [69] Bridgman, P. W., Rough compressions of 177 substances to 40,000 kg/cm<sup>2</sup>, *Proc. Am. Acad. Arts Sci.* **76**, 71-87 (1948).
- [70] Grüneisen, E., Die elastischen Konstanten der Metalle bei kleinen Deformationen, *Ann. Phys.* **22**, 801-851 (1907).
- [71] Richards, T. W., Die Zusammendrückbarkeit der Elemente, *Z. Elektrochem.* **13**, 519-520 (1907).
- [72] Adams, L. H., Williamson, E. D., and Johnston, J., The determination of the compressibility of solids at high pressures, *J. Amer. Chem. Soc.* **41**, 12-42 (1919).
- [73] Sieglerschmidt, H., Bestimmung der Poissonschen Zahl  $\mu$  gewalzter Zinkbleche, *Z. Metallk.* **24**, 55-56 (1932).
- [74] Guillet, L., *Le Genie civil* **116**, 29 (1940). Cited in Ref. 75.
- [75] Koster, W., Die Temperaturabhängigkeit des Elastizitätsmoduls reiner Metalle, *Z. Metallk.* **39**, 1-9 (1948).
- [76] Peselnick, L., and Meister, R., Variational method of determining effective moduli of polycrystals: (a) hexagonal symmetry, (b) trigonal symmetry, *J. Appl. Phys.* **36**, 2879-2883 (1965).
- [77] Reuss, A., Calculation of the elastic limit of solid solutions on the basis of plasticity conditions for single crystals, *Z. Angew. Math. Mech.* **9**, 49-58 (1929).
- [78] Grüneisen, E., and Goens, E., Untersuchungen an Metallkristallen. II. Spezifische Wärme und elektrischer Widerstand von Zink und Cadmium, *Z. Physik* **26**, 250-273 (1924).
- [79] Clusius, K., and Harteck, P., *Z. Phys. Chem.* **134**, 243 (1928). Reported in Ref. 100.
- [80] Keesom, P. H., and van den Ende, J. M., *Proc. Amst. Akad. Sci.* **35**, 143 (1932). Reported in Ref. 87.
- [81] Keesom, W. H., and Haantjes, J., *Physica* **2**, 986 (1935). Reported in Ref. 98.
- [82] Silvidi, A. A., and Daunt, J. G., Electronic specific heats in tungsten and zinc, *Phys. Rev.* **77**, 125-129 (1950).
- [83] Post, E. J., On the characteristic temperatures of single crystals and the dispersion of the "Debye heat waves," *Can. J. Phys.* **31**, 112-119 (1953).
- [84] Blackman, M., The specific heat of solids, in *Handbuch der Physik*, Vol. VII-I, S. Flugge, ed., Springer-Verlag, Berlin (1955).
- [85] Smith, P. L., The specific heats of magnesium and zinc, *Phil. Mag.* **46**, 744-750 (1955).
- [86] Betts, D. D., Bhatia, A. B., and Horton, G. K., Debye characteristic temperatures of certain noncubic crystals, *Phys. Rev.* **104**, 43-47 (1956).
- [87] Keesom, P. H., and Pearlman, N., Low temperature heat capacity of solids, in *Handbuch der Physik*, Vol. XIV-I, S. Flugge, ed., Springer-Verlag, Berlin (1956).
- [88] Alers, G. A., and Neighbors, J. R., Comparison of the Debye  $\theta$  determined from elastic constants and calorimetry, *Rev. Mod. Phys.* **31**, 675-680 (1959).
- [89] Seidel, G., and Keesom, P. H., Specific heat of gallium and zinc in the normal and superconducting states, *Phys. Rev.* **112**, 1083-1088 (1958).
- [90] Zavaritskii, N. V., Investigation of the thermal properties of superconductors. II, *J. Exptl. Theor. Phys. (USSR)* **34**, 1116-1124 (1958).
- [91] Wolcott, N. M., Debye  $\theta$  of hexagonal crystals at 0 K, *J. Chem. Phys.* **31**, 536-540 (1959).
- [92] Srinivasan, T. M., Lattice and electronic specific heats of zinc and cadmium, *Proc. Indian Acad. Sci.* **49**, 61-65 (1959).
- [93] Zimmerman, J. E., and Crane, L. T., Anomalous lattice specific heat of gold and zinc at liquid helium temperatures, *Phys. Rev.* **126**, 513-516 (1962).
- [94] Anderson, O. L., A simplified method for calculating the Debye temperature from elastic constants, *J. Phys. Chem. Solids* **24**, 909-917 (1963).
- [95] Anderson, O. L., Determination and some uses of isotropic elastic constants of polycrystalline aggregates using single-crystal data, in *Physical Acoustics*, Vol. III-B, W. P. Mason, ed., Academic, New York (1965).
- [96] Reddy, P. J., Calculation of the Debye temperatures of crystals, *Physica* **29**, 63-66 (1963).
- [97] Robie, R. A., and Edwards, J. L., Some Debye temperatures from single-crystal elastic constant data, *J. Appl. Phys.* **37**, 2659-2663 (1966).
- [98] Holm, M. W., Debye characteristic temperatures table and bibliography, AEC Report IDO-16399 (1957).
- [99] Boas, W., *Physics of Metals and Alloys*, Melbourne U. P., Carlton, Victoria (1947).
- [100] Blackman, M., The theory of the specific heat of solids, *Rep. Prog. Phys.* **8**, 11-30 (1941).
- [101] Simmons, G., and Wang, H., *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook*, M.I.T. Press, Cambridge, Mass. (1971).