

Thermal Expansion of Single and Optically Mosaic Zinc Crystals

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Thermal expansions of sixteen zinc single crystals have been measured in the temperature range, 25° to 100°C by an optical lever method. The dependence on orientation followed the expected cosine-squared symmetry relation. The principal coefficients, parallel and perpendicular to the hexagonal axis, were found to be: $\alpha_0 = 64.2$ and $\alpha_{90} = 14.1 \times 10^{-6}$ per degree C. Slight differences in purity did not affect the values of the expansion coefficients, nor did optically mosaic crystals differ from true singles. Permanent strain lowered the coefficients slightly.

SEVERAL previous determinations of the linear coefficients of expansion of zinc single crystals have been made, but because of poor agreement in these, new measurements were thought desirable. Grüneisen and Goens¹ measured directly the thermal expansion of two crystals of very different orientation and by extrapolation obtained values of the two principal coefficients, α_0 and α_{90} . Their results covered a considerable temperature range. Bridgman² also made measurements on two crystals, using an optical lever system and crystals approximately 2.5 cm in length. His temperature range was from 15° to 25°C. His results were approximately ten percent lower than those of Grüneisen and Goens for the same region. Crystal lattice measurements have been made by x-ray methods, and the so-called "lattice-coefficients" calculated, by McLennan and Monkman³ at low temperatures and Owen and Yates⁴ from 20° to 100°C. Measurements by Austin,⁵ who used an interferometer method and very small crystals, yielded results varying greatly from those of previous determinations. He used five single crystals in his temperature range of from 0° to 350°C.

An optical lever system was used in the present work because of its extreme sensitivity, accuracy, and ease of use. Not only is a large magnification easily obtainable, but there is an additional advantage due to the fact that long specimens can be used. The crystals were from nine to twelve centimeters in length. The apparatus was de-

signed also to do away with any excess handling of the crystals previous to the measurement, such

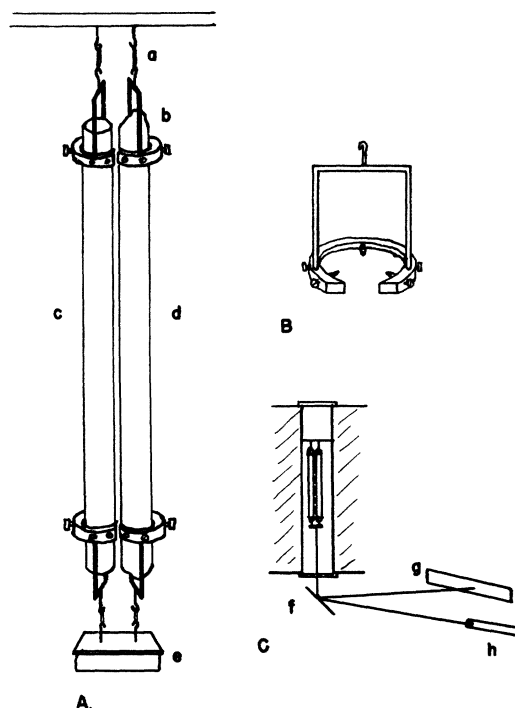


FIG. 1. Arrangement of apparatus. A. Crystal, *d*, and quartz rod, *c*, suspended side by side; mirror, *e*. B. Detail of collar. C. Sketch of complete assembly.

as cleaving, or smoothing of the surface. Since it was the differential expansion between a fused quartz rod and the zinc crystals that was measured, the value of α for the zinc was obtained by adding to the observed value the linear expansion coefficient of the quartz, 0.5×10^{-6} per degree C. The apparatus is shown in Fig. 1. Small collars *B* were fitted to the crystals and held by three small set screws. A collar was put over each end of the

¹ E. Grüneisen and E. Goens, *Zeits. f. Physik* **29**, 141 (1924).

² P. W. Bridgman, *Proc. Am. Acad.* **60**, 305 (1925).

³ J. C. McLennan and R. J. Monkman, *Trans. Roy. Soc. Can.* [3] **23**, 255 (1929).

⁴ E. A. Owen and E. L. Yates, *Phil. Mag.* **17**, 113 (1934).

⁵ J. B. Austin, *Physics* **3**, 240 (1932).

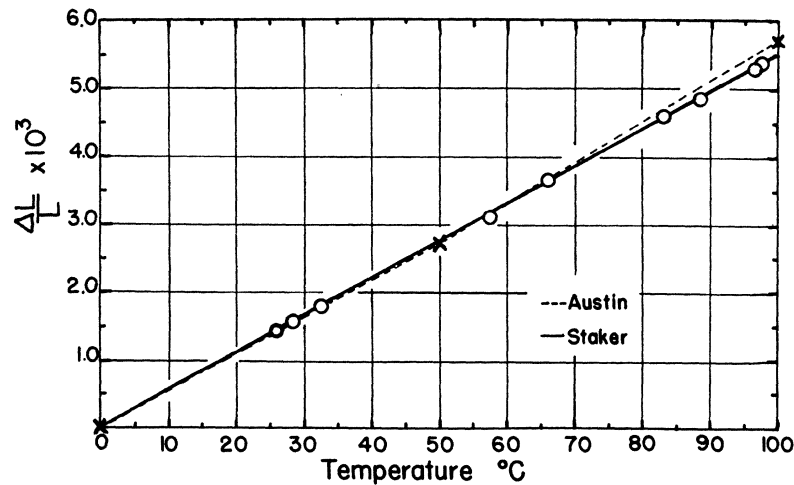


FIG. 2. Change in length per unit length at 0°C, as function of temperature. The x's and broken line are Austin's data for a 0° crystal. The circles and solid line are the writer's for a 24.4° crystal.

crystal *d* Fig. 1A, and by means of a small hook and small wire loops *a* the crystal was suspended from a cross-bar in the furnace. The fused quartz rod *c* was suspended in like manner. The collars were flattened on one side in order that the crystal and quartz rod could hang as close as possible without touching. From the hooks on the collars at the lower end of the crystal and quartz rod there was hung a small plane mirror, *e*, by means of loops attached to hooks in the mirror holder. The image of a scale *g* Fig. 1C, was observed in the mirror by means of a telescope *h*. A magnification of 480 was realized with a light path from scale to mirror of 234 cm and lever arm of mirror equal to 0.975 cm. The bottom of the furnace had a glass plate covering it. Below this was a plane mirror *f* set at 45° with the horizontal to reflect the light in from the scale and then out again to the telescope. With this magnification there was at the highest temperature, a total scale deflection of approximately 5 cm for the high orientation crystals and as much as 20 cm for the low orientation crystals. This corresponds to a total expansion of about 0.1 mm for the high orientation crystals and 0.5 mm for low orientations. If we assume that the scale could be read accurately to 0.2 mm, the corresponding error would be 0.4 percent for the high orientation crystals, or 0.1 percent for the low

orientations. Otherwise stated, the $\Delta L/L$ corresponding to 0.2 mm scale reading is 4×10^{-6} .

The collars and all metal parts used were made symmetrical in order to avoid any possible error. To remove any possibility of extraneous effects due to uneven expansion of the furnace and base, the average of two runs was used between which the crystal and quartz rod were interchanged.

Chromel-alumel thermocouples were used with a Leeds and Northrup type K potentiometer to determine the temperature. Because of the length

TABLE I. Summary of results.

No.	Material	Condition	Orientation	$\cos^2 \theta$	Observed α_θ ($\times 10^6$)	Calculated* α_θ ($\times 10^6$)	Deviation ($\times 10^6$)
1	BH ³	mosaic	90.0°	0.000	13.9	14.1	0.2
2	BH ³	mosaic	84.1	.0106	14.2	14.6	0.4
3	BH ³ +Cd	single	80.3	.0284	15.7	15.5	0.2
4	BH ³ +Cd	single	76.0	.0586	17.0	17.0	0.0
5	BH ³ +Cd	mosaic	75.5	.0625	17.05	17.2	0.15
6	BH ³	mosaic	72.3	.0924	18.7	18.7	0.0
7	BH ³	single	70.6	.110	19.5	19.6	0.1
8	BH ³	single	58.5	.273	27.7	27.8	0.1
9	BH ³ +Cd	single	51.9	.381	33.2	33.2	0.0
10	HH	mosaic	44.5	.510	39.2	39.6	0.4
11	BH ²	single	28.2	.776	52.5	52.9	0.4
12	BH ²	single	27.0	.794	53.8	53.9	0.1
13	BH ²	single	25.1	.820	54.9	55.2	0.3
14	BH ²	single	24.4	.829	55.5	55.6	0.1
15	BH ²	mosaic	23.7	.838	57.1	56.0	1.1
16	BH ²	single	22.0	.859	57.8	57.1	0.7
9**	BH ³ +Cd	single	51.9	.381	31.1	33.2	2.1
17**	BH ³	mosaic	55.3	.324	28.1	30.3	2.2
17***	BH ³	mosaic	55.3	.324	29.1	30.3	1.2

* $\alpha_\theta = \alpha_{100} + (\alpha_0 - \alpha_{100}) \cos^2 \theta$; $\alpha_\theta = (14.1 + 50.1 \cos^2 \theta) \times 10^{-6}$.

** Strained.

*** Annealed.

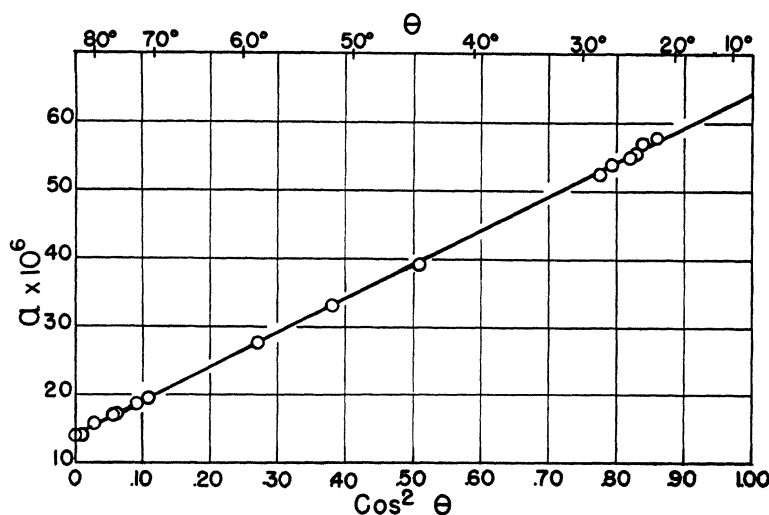


FIG. 3. Mean coefficients of expansion (25°–100°C) of sixteen crystals as function of square of cosine of orientation angle.

of the specimen, two thermojunctions were used, one placed near each collar on the crystal. The temperatures at these two points rarely differed by more than 0.25°C, and since different localities along the crystal showed no greater variation, the average of these two points was considered to be the temperature of the specimen.

Each run consisted of readings taken at five or six temperatures from room temperature up to 100°C and back again. Each rising temperature reading was made by increasing the furnace current an appropriate amount and then waiting until temperature equilibrium was surely reached, a matter of several hours. Readings with falling temperatures were taken similarly. The two sets

of readings, when plotted, lay within experimental error, on the same straight line. (See Fig. 2.) The expansion coefficient was computed from the slope of this line. A complete run took about twenty-four hours.

Measurements were made on sixteen crystals of various lots of zinc. Details are given in the second, third, and fourth columns of Table I. The designations BH² and BH³ refer to two lots of Bunker Hill⁶ zinc; BH³+Cd means that approximately 0.2 percent cadmium was added to the zinc; HH stands for Horsehead special zinc;⁶ mosaic indicates that the crystals were "optical mosaics."⁷ The specimens made of BH³ zinc were circular in cross section and were grown by a modified Bridgman method, as described by Good.⁸ The BH² and HH specimens were trapezoidal in cross section and were grown by Professor E. P. T. Tyndall by the method described by Cinnamon.⁹

The measurements are summarized in Table I and are shown graphically in Fig. 3. The inter-

TABLE II. Mean principal expansion coefficients.

Observer	α_{90}^0 ($\times 10^6$)	α_0^0 ($\times 10^6$)	Method	T (°C)
Staker	14.1	64.2	Optical lever	25 to 100
Grüneisen and Goens	14.1	63.9	Direct measure	20 to 100
Bridgman	12.6	57.4	Optical lever	15 to 25
Owen and Yates	14.3	60.8	X-ray	20 to 100
Austin	19.0	57.0	Interferometer	0 to 100
Grüneisen and Goens	9.4	65.0	Direct measure	20 to -180
McLennan and Monkman	11.3	49.5	X-ray	18 to -190

⁶ Bunker Hill and Horsehead special are commercial zincs of very high purity (about 99.99 percent zinc). For some estimate of impurities in BH² and HH see H. E. Way, *Phys. Rev.* **50**, 1181 (1936) and A. W. Hanson, *Phys. Rev.* **45**, 324 (1934).

⁷ H. K. Schilling, *Physics* **5**, 1 (1934), and W. J. Poppy, *Phys. Rev.* **46**, 815 (1934).

⁸ W. A. Good, *Phys. Rev.* **60**, 605 (1941).

⁹ C. A. Cinnamon, *Rev. Sci. Inst.* **5**, 187 (1934).

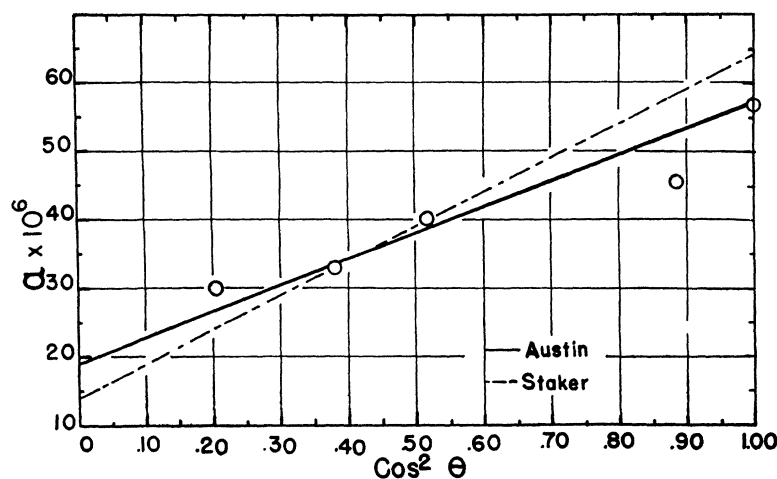


FIG. 4. Mean coefficient (0° - 100°C) as determined by Austin as function of square of cosine of orientation angle. The dotted line is the writer's line of Fig. 3.

cepts of the line, 14.1×10^{-6} and 64.2×10^{-6} , are α_{90} and α_0 , respectively. The line was fitted to the data by the method of least squares. It may be seen in Table I that the observed values lie very close to the line. The largest deviation is 1.1×10^{-6} for crystal No. 15. The mean (absolute) deviation is 0.27. No significant difference is evident between the various lots of zinc nor for the crystals which contained cadmium, nor for those which were optically mosaic.

The coefficient of expansion for a crystal (No. 17) known to have been strained was also found. It was 28.1×10^{-6} , but, after annealing, rose to 29.1×10^{-6} . In order to get an independent check on this supposed effect of strain, another crystal (No. 9), which had originally given a value falling on the line, was strained. After straining, it gave a value of 31.1×10^{-6} instead of the original 33.2×10^{-6} .

The present and previous results are summarized in Table II by giving the two mean principal thermal expansion coefficients, α_0 and α_{90} , for the temperature ranges indicated. The writer's results agree most closely with those of Grüneisen and Goens. Although Bridgman's results are lower, the ratio of principal coefficients is the same ($\alpha_0/\alpha_{90}=4.55$). The fairly good agreement with Owen and Yates seems to indicate that the lattice expansion and macroscopic expansion are not significantly different. Moreover, what difference there is may perhaps be

ascribed to the fact that the x-ray measurements were made on filings of the polycrystalline material and there might well be, under such circumstances, enough constraint to reduce the large expansion parallel to the axis, particularly as this is the direction of lowest Young's modulus. The present results do not throw any direct light on the large disagreement of McLennan and Monkman with Grüneisen and Goens for low temperatures. The writer's disagreement with Austin, whose work was done by a very sensitive method and apparently with great care, warrants some discussion. Austin's data for the temperature range 0° to 100°C are plotted in Fig. 4. By comparison with Fig. 3, it is seen that his results are more scattered than the writer's. Austin also considered his results to show that the mean coefficients of expansion, taken for successive 50° intervals, alternately increased and decreased. The writer found no such effect between room temperature and 100°C . This is shown in Fig. 2, in which the three points indicated by x 's are Austin's values of $\Delta L/L$ for a zero-degree orientation crystal. These determine two straight lines with a noticeable difference in slope, whereas the writer's points (0) for a 24° crystal lie, within experimental error, on a single straight line. No run on any crystal showed any sign of a noticeable difference in slope between the low and high temperature ends. The writer believes that the two largest sources of error in Austin's work were

the use of such short lengths and the complicated method used to measure temperature. His measurements were of the transverse expansion on crystal rods 2.5 mm in diameter.

In conclusion, the writer wishes to express his sincere appreciation to Professor E. P. T. Tyndall for suggesting this problem and for his encouragement and advice throughout the work.

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Field Emission from Tungsten and Thoriated Tungsten Single Crystals*

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A reproducible time sequence of different pattern types has been found to appear in electron projector images of field emission from tungsten single crystals when the crystals are kept at temperatures above 1100°K. These pattern types, some of which have been observed before and attributed to migrations of surface tungsten atoms, can best be explained (with a single possible exception) as the result of rearrangement of adsorbed gas atoms on certain crystallographic surface areas under the influence of temperature and field. Their classification by means of their relation to surface conditions provides a sensitive test for a clean tungsten surface. The relative variation of emission intensity with crystallographic direction observed in thermionic emission is duplicated in field emission from clean tungsten, but the magnitudes of the variations are greater in field emission. These magnitudes seem to be greater than can be accounted for by the dependence of field emission on the exponential third power of work

function which is indicated by some experiments. Such experiments in turn are at variance with theory, which predicts only an exponential three-halves power dependence. Attempts to extend electron projector methods of investigation to the simple composite surface of thorium on tungsten have uncovered no positive tests for surface conditions. Distinctly different types of field emission patterns were obtained from thoriated points formed from thoria-incorporated tungsten wire than from points of pure tungsten upon which thorium was evaporated externally. These differences disappeared, however, when the former patterns transformed into the latter after outgassing of the points for one or two hours at temperatures between 2700°K and 2900°K. In this final pattern, thorium adsorbs chiefly on the regions around but not including the 100 direction, and on a triangular region about and including the 111 direction. Once deposited, the thorium could not be completely removed from the tungsten surface.

INTRODUCTION

WHEN applied to the Fermi-Sommerfeld picture of a metal, the conception of wave mechanical penetration by electrons of a surface potential barrier lowered and thinned by an intense, externally applied, electrostatic field leads to the field emission equation first derived¹ by Fowler and Nordheim:^{2,3}

$$J = 1.55 \times 10^{-6} (F^2/w) 10^{-2.98 \times 10^7 (w^3/F) \phi(y)}. \quad (1)$$

In this equation J is the field emission current density in amperes per square centimeter, F the

surface potential gradient in volts per centimeter, w the work function⁴ in electron volts, $y = 3.62 \times 10^{-4} (F^3/w)$, and $\phi(y)$ is a function containing the ratio of two elliptic integrals which has been tabulated for values of y from 0 to 1 by Nordheim.³

Although the general features of Eq. (1) have been confirmed experimentally,⁵⁻⁸ difficulties resulting from the extremely high surface fields required have prevented conclusive establish-

* Part of a thesis presented for the degree of Doctor of Science, from The Department of Physics, Massachusetts Institute of Technology, October, 1940.

¹ Errors in the original derivations may be avoided by consulting the complete derivation given in A. Sommerfeld and H. A. Bethe, *Handbuch der Physik* (1934), Vol. 24, Part 2, Sec. 3, Art. 19, p. 436.

² R. H. Fowler and L. Nordheim, *Proc. Roy. Soc. A* **119**, 173 (1928).

³ L. Nordheim, *Proc. Roy. Soc. A* **121**, 626 (1928).

⁴ Defined as the difference in potential energy of an electron in the highest occupied energy level allowed by quantum statistics at 0°K, and that of the electron when removed from the metal and carried to a distance large compared to the lattice constant, so that the image force becomes practically zero, but small compared to the dimensions of the crystal face.

⁵ E. W. Müller, *Zeits. f. Physik* **102**, 734 (1936).

⁶ J. E. Henderson and R. K. Dahlstrom, *Phys. Rev.* **55**, 473 (1939).

⁷ F. R. Abbott and J. E. Henderson, *Phys. Rev.* **56**, 113 (1939).

⁸ G. M. Fleming and J. E. Henderson, *Phys. Rev.* **58**, 887 (1940).