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Temperature Dependence of Young's Modulus of Beta-Brass Single Crystals

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Young's modulus of seven single crystals of beta-brass has been measured as a function of temperature from 25°C to 505°C for the purpose of studying the order-disorder phenomenon. The method used is that of the composite piezoelectric oscillator. The reciprocal of Young's modulus is linearly related to the orientation function at all temperatures. The maximum and minimum values of the reciprocal of Young's modulus, $1/E_{[100]}$ and $1/E_{[111]}$, are 3.881 and 0.475×10^{-12} at room temperature and 4.970 and 0.583×10^{-12} cm^2/dyne at the critical temperature (468°C). The elastic anisotropy, given by $E_{[111]}/E_{[100]}$, has the value, 8.2, at room temperature, decreases to a minimum, 7.2, at 300°C, and again increases to 8.6 at the critical temperature. Plots of the reciprocal of Young's modulus in three principal directions, [100], [110], and [111], show that the effect of disorder is mainly felt in the first two directions, while in the third direction the elasticity shows an approximately linear increase with increasing temperature. Before disorder sets in the elasticity in the [100] direction decreases with increasing temperature, contrary to the usual behavior of elastic materials.

INTRODUCTION

During the past few years experiments on the change in physical properties of certain ordered alloys as they go through the order-disorder transition have been very fruitful, and the results are in close agreement with theoretical developments in that field. Comprehensive reviews of both theory and experiment have been given by Nix and Shockley,[1] Borelius,[2] and Schottky.[3] While most of the early work was done with polycrystalline material, studies on single crystal specimens have been made recently. Webb[4] has reported a detailed study of the resistivity and thermoelectric power of beta-brass both as a function of temperature and composition. Siegel[5] has obtained the temperature dependence of the principal elastic moduli of Cu_3Au from measurements made on single crystals of the material.

On the theoretical side,[6] no complete treatment has been given of the dependence of elastic properties on the order-disorder transition. It is experimentally established[5,7] that some connection exists, and it is hoped that the present research may throw some light upon the exact nature of this connection and stimulate further theoretical developments.

One of the simplest alloys showing an order-disorder transition is beta-brass. Its crystal structure is body-centered cubic. In the ordered state, zinc atoms occupy cube corners and copper atoms, cube centers, or vice versa. In the disordered state either kind of atom has an equal probability of being in either lattice position. This alloy was chosen for study because Webb's[4] work indicated that a further study of the elasticity of single crystals of this material would be interesting. He found beta-brass to be elastically highly anisotropic in that Young's modulus varied markedly with direction in the crystal lattice. In the present investigation, the anisotropic character of this material was studied more closely at room temperature. Further, the effect of disorder upon Young's modulus for various directions in the crystal lattice was studied.

PREPARATION OF CRYSTALS

The material from which the crystals were grown was supplied through the kindness of Dr. Cyril S. Smith, research metallurgist for the American Brass Company, Waterbury, Connecticut. The accompanying chemical analysis showed the following weight percents: Cu, 51.78; Pb, 0.02; Fe, 0.01; Zn, 48.29 (by difference).

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[1] F. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938).
[2] G. Borelius, Zeits. f. Elektrochemie **45**, 16 (1938).
[3] W. Schottky, Zeits. f. Elektrochemie **45**, 33 (1938).
[4] W. Webb, Phys. Rev. **55**, 297 (1939).
[5] S. Siegel, Phys. Rev. **57**, 537 (1940).
[6] W. Bragg and E. Williams, Proc. Roy. Soc. **A144**, 340 (1934); H. Bethe, Proc. Roy. Soc. **A150**, 552 (1935); R. Peierls, Proc. Roy. Soc. **A154**, 207 (1936).
[7] W. Köster, discussion of paper by Borelius, reference 2.

Neglecting the small impurities, this corresponds to atomic percents of 52.8 and 47.2 for the copper and zinc, respectively. The crystals were grown by Bridgman's[8] method. Instead of making a preliminary polycrystalline casting, a machined blank of the desired size and shape was prepared. It was then coated with several layers of Insalute cement to make an individual mold. In this way crystals with accurately determined dimensions and smooth surfaces were obtained. The blanks were 3 mm square, about 6 cm long and tapered to a point at one end so as to increase the likelihood of a single crystal starting.

Since single crystals of this material are relatively easy to grow, no detailed study was made of growth conditions. It was found, however, that, in general, slower rates of growth produced crystals having a lower orientation function. The rates of growth varied from about 6 cm/hr. to 30 cm/hr. through a temperature gradient of about 75 deg. C/cm. Some twenty-five crystals were grown, approximately fifty percent of which were found to be satisfactory for further use.

ORIENTATION AND ORIENTATION FUNCTION

The orientation function, $F(l,m,n)$, upon which Young's modulus in any direction depends is

$$F(l,m,n)=l^2m^2+l^2n^2+m^2n^2, \qquad (1)$$

in which l, m, and n are the direction cosines of the length of the specimen with respect to the crystallographic axes. The orientation was determined as described by Webb.[4] Either three or four reflections were used, which gave three or six partially dependent values of l, m, and n. Values of the orientation function calculated from different sets were found to agree within about one percent. The largest error introduced in the measurement results from the inability to set the crystal in the goniometer so that its length is exactly perpendicular to the incident light beam. By removing the crystal, rotating it end for end, and remeasuring the angles, a considerable amount of this error was eliminated. In every case the two different settings gave angles which agreed within one or two degrees. In all cases the crystals exhibited bright reflections when removed from the mold without further treatment. Practically all the observed reflections were from $\{110\}$ and $\{111\}$ planes.

MEASUREMENT OF YOUNG'S MODULUS

Young's modulus was measured by a dynamic method which has been used extensively and adequately described.[9] Longitudinal vibrations were set up in the crystal specimen by means of a suitably cut square-cross-section quartz rod cemented to it with Insalute cement. Aluminum leaf electrodes were attached to the quartz, and the composite bar was placed on a holder, consisting of a transite block about $6''\times1''\times\frac{1}{2}''$, upon which were mounted two lava knife edges for supporting the bar close to its nodes of vibration. For temperature measurements, three thermocouples[10] were mounted at equally spaced intervals along the length of the holder. As regards frequency the crystals were matched in the usual way. The frequency standardization was made by means of a piezoelectric clock in a manner described by Quimby,[11] and the frequency measurements are believed to be accurate to one part in 100,000.

The runs above room temperature were made by placing the composite oscillator and its holder in a heavy iron cylinder near the middle of an Alundum-cored furnace. The furnace windings were so arranged that the temperature difference over the length of the specimen did not exceed one or two degrees. Readings were taken with both increasing and decreasing temperature. In most cases the crystal was run back and forth through the critical region two or three times. To eliminate lag between the temperature measured by the thermocouples and the actual temperature of the crystal, successive readings were taken as follows. The furnace current was changed slightly and sufficient time allowed to elapse until a steady state ensued, after which the resonance frequency and temperature were measured. At lower temperatures the rate of

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[8] P. Bridgman, Proc. Am. Acad. **60**, 305 (1925).

[9] S. L. Quimby, Phys. Rev. **25**, 558 (1925); J. Zacharias, Phys. Rev. **44**, 116 (1933); L. Balamuth, Phys. Rev. **45**, 715 (1934); F. Rose, Phys. Rev. **49**, 50 (1936).

[10] Carefully calibrated Chromel-Alumel thermocouples were used in conjunction with a Leeds and Northrup type K potentiometer.

[11] S. L. Quimby, Phys. Rev. **39**, 345 (1932). The writer is indebted to Professor Quimby for many of the circuit diagrams used and many helpful suggestions.

heating or cooling was about 25°C per hour. In the neighborhood of the critical temperature the rate was less. Measurements made with increasing and decreasing temperatures agreed so closely that it was certain that the lag was eliminated and that the thermocouples measured the true temperature of the specimen. The relaxation time of beta-brass is known to be so short that no lag due to departure from an equilibrium condition needed to be guarded against.

Young's modulus along the axis of a bar at temperature T, is related to the resonance frequency, f, of the brass specimen by the formula,[5]

$$E=4\rho_{25}L^2{}_{25}f\left(\frac{L_{25}}{L_T}\right)\left[1+\frac{1}{2}\frac{A\bar{\sigma}^2n^2}{L^2{}_{25}}\right], \tag{2}$$

where ρ_{25} and L_{25} are the density and lengths of the bar at 25°C, respectively, $\bar{\sigma}$ is the average Poisson's ratio, n is the approximate number of half-waves in the metal crystal, and A is the area of the cross section. The term in the brackets is a correction due to the lateral motion. It is so near unity that in the present calculation it has been taken as one. In order to get L_T from L_{25}, values of the coefficient of thermal expansion of polycrystalline beta-brass, determined by Merica and Schad,[12] were used.

A comparator was used to measure the lengths of the specimens at room temperature. Eight measurements were taken on each crystal and the uncertainty in length is believed not to exceed 0.1 percent.

The density at 25°C was determined by the method of hydrostatic weighing. The value, 8.35 g per cc, so obtained is, judging by the deviations of individual readings from the mean, accurate within 0.5 percent.

TABLE I. *Summary of data for seven single crystals at room temperature.*

CRYSTAL	$F(l, m, n)$	$1/E\times10^{12}$ CM²/DYNE	$E\times10^{-11}$ DYNE/CM²
6	0.0220	3.664	2.729
7	0.0780	3.082	3.245
24	0.1648	2.202	4.541
22	0.1868	1.938	5.160
11	0.2439	1.418	7.052
16	0.2665	1.148	8.711
12	0.2756	1.069	9.355

RESULTS AT ROOM TEMPERATURE

Table I gives results for room temperature. Similar data were obtained for temperatures ranging from room temperature to above the critical temperature for order.

The principal elastic coefficients,[13] s_{11}, s_{12}, and s_{44} of a cubic crystal are related to Young's modulus by the formula

$$1/E=s_{11}-2sF(l,m,n), \tag{3}$$

where $s=s_{11}-s_{12}-\frac{1}{2}s_{44}$

and $F(l,m,n)$ is the orientation function previously given. Equation (3) shows that a plot of $1/E$ against $F(l,m,n)$ should be a straight line. From it, one of the elastic coefficients, s_{11}, and a relationship between the other two, namely, $(2s_{12}+s_{44})$, may be determined. Quantities of the most interest physically, perhaps, are the reciprocals of Young's modulus in the [100], [110], and [111] directions. The first of these is the elastic coefficient, s_{11}, and corresponds to a direction along the cube edge of the crystal. The second corresponds, among other directions, to the direction along a face diagonal, and the third to a direction along the cube diagonal. Equation (3) yields $1/E_{[111]}$, $1/E_{[110]}$, and $1/E_{[100]}$ $(=s_{11})$ upon substitution of $\frac{1}{3}$, $\frac{1}{4}$, and zero, respectively, for the orientation function.

The reciprocal of Young's modulus of each of the seven crystals was plotted against its orientation function for about thirty different temperatures. At each temperature, a straight line was fitted to the points by the method of least squares. For room temperature, the appropriate values from Table I are shown plotted as curve B, Fig. 1.

Insofar as the writer knowns, the only other data available on the elastic properties of beta-brass single crystals are those of Webb.[4] He states that his determination can hardly be con-

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[12] P. Merica and L. Schad, Bull. Bur. Stand. **14**, 571 (1918). The values they give are 22.8, 19.4, 23.5, 27.5, 39.2, and 26.9×10^{-6} per deg. C for the temperature ranges 25–100, 100–200, 200–300, 300–400, 400–469, and 470–510 degrees C, respectively.

[13] Schmid and Boas, *Struktur und Eigenschaften der Materie XVII, Kristallplastizität*, p. 23. These s_{11}, s_{12}, etc. are variously known as elastic constants, moduli, coefficients, parameters, etc. The writer will adopt the terminology used by Schmid and Boas and call them coefficients. The term "modulus" does not seem so happy in that, dimensionally, the s's are strain/stress, whereas modulus is commonly used for stress/strain.

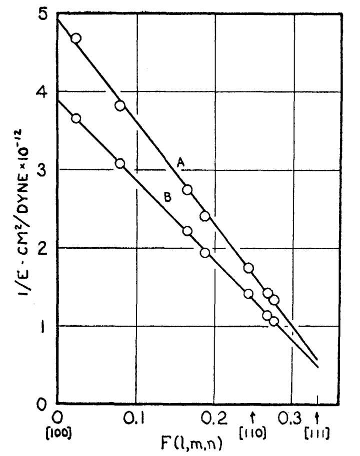

FIG. 1. $1/E$ against orientation function. Curve B at room temperature. Curve A at 466°C, temperature at which anisotropy in Young's modulus is a maximum.

sidered complete or of very high precision chiefly because of the irregularity of his specimens. In the final fitting of the curve, Webb ignored two of his points solely because they did not seem to agree with the rest of the observations. To the writer, it seems preferable to include these points, and a least-square fit has been made on this basis. Table II compares Webb's values as given by him and as corrected, with the writer's.[14] The corrected values are seen to be in better agreement with the writer's.

The unusual degree of anisotropy in Young's modulus, as shown by the large ratio of maximum to minimum modulus in the [111] and [100] directions, respectively, was noted by Webb.[4] The writer's results check Webb's reasonably well. Webb suggested further, that this high degree of anisotropy might disappear in the disordered state.[15] The writer's results provide a test of this hypothesis. It was found to be incorrect as will appear later.

DEPENDENCE ON TEMPERATURE

The results of the measurements at elevated temperatures are presented in summarized form in Table III and shown graphically in the curves of Figs. 2 and 3, which are plots of reciprocals of Young's modulus in three directions in the crystal, [100], [110], and [111]. The behavior of these three curves is most conveniently described by dividing the temperature range into the four rather arbitrary regions, 25°C–150°C, 150°C–468°C, 468°C–469°C, and 470°C–510°C.

In the first of these regions, specific heat[16] and resistivity[4] measurements indicate that very little, if any, disordering sets in. It might be expected, then, that any change in elasticity would be the linear increase in s_{11}, s_{12}, etc. observed in most substances. It is apparent from the curves, that, although the part below 150°C is approximately straight, the slope depends entirely upon the orientation of the crystal. In the [111] direction, the behavior of Young's modulus is like that for an isotropic solid (Fig. 3). In the [110] direction and other directions with the same orientation function (see lower curve in Fig. 2) there is almost zero change in $1/E$. Qualitatively, this is in agreement with Köster,[7] who found very little change in Young's modulus with temperature over this temperature range for polycrystalline beta-brass, since a specimen consisting of randomly oriented crystals would

TABLE II. *Comparison with Webb's results.*

	$1/E_{[100]}\times 10^{12}$ CM²/DYNE	$1/E_{[110]}\times 10^{12}$ CM²/DYNE	$1/E_{[111]}\times 10^{12}$ CM²/DYNE	$(2s_{12}+s_{44})\times 10^{12}$ CM²/DYNE	$E_{[111]}/E_{[100]}$
Webb	4.48	1.53	0.50	−2.8	8.9
Webb (corrected)	4.28	1.48	0.54	−2.7	7.9
Rinehart	3.88	1.33	0.48	−2.5	8.2

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[14] It must be remembered, however, that the present method is a dynamic one and it is the adiabatic Young's modulus which is obtained, while the static method used by Webb gives the isothermal value. The difference between the two is easily calculated (see Voigt, *Lehrbuch der Kristallphysik*, p. 789) and is found to be much too small to account for the difference between Webb's and the writer's values. Another reason for the discrepancy may lie in the fact that Webb's crystals varied widely in composition, but neither the writer nor Webb was able to find from his data any direct correlation between the composition and the value of Young's modulus.

[15] Webb's argument was that, while the large anisotropy at room temperature might easily be attributed to a difference in binding energy between like atoms and unlike atoms, in the disordered state, the various kinds of possible bindings might be expected to give a sort of average result, and hence make the crystal more nearly isotropic.

[16] H. Moser, Physik. Zeits. **37**, 737 (1936).

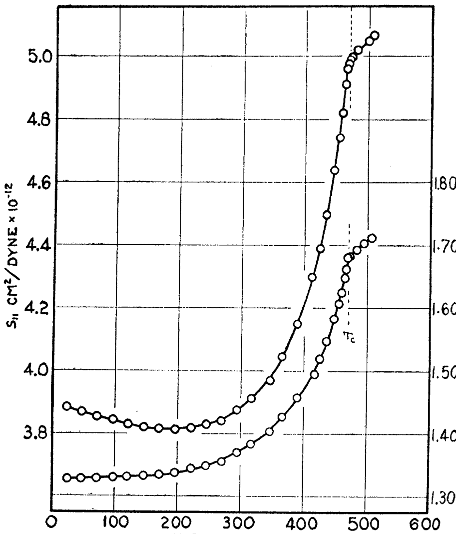

FIG. 2. $1/E$ against temperature. Lower curve, $1/E_{[110]}$. Upper curve, $1/E_{[100]}$.

TABLE III. *Reciprocal of Young's modulus in principal directions.*

TEMP. °C	$1/E_{[100]}\times10^{12}$ CM²/DYNE	$1/E_{[110]}\times10^{12}$ CM²/DYNE	$1/E_{[111]}\times10^{12}$ CM²/DYNE
24	3.881	1.326	0.475
48	3.865	1.326	.480
72	3.850	1.327	.486
96	3.841	1.327	.489
121	3.829	1.328	.495
145	3.817	1.330	.502
170	3.814	1.333	.506
195	3.810	1.337	.512
220	3.815	1.342	.517
245	3.826	1.348	.522
269	3.838	1.354	.526
293	3.871	1.368	.534
317	3.909	1.383	.541
341	3.967	1.402	.546
365	4.042	1.426	.554
389	4.148	1.457	.560
412	4.296	1.495	.561
424	4.386	1.519	.563
436	4.492	1.547	.565
448	4.637	1.581	.562
455	4.738	1.606	.561
459	4.816	1.623	.559
464	4.908	1.647	.560
466	4.959	1.662	.563
468(T_c)	4.970	1.680	.583
471	4.987	1.682	.580
473	4.993	1.683	.579
483	5.020	1.692	.583
495	5.045	1.702	.588
506	5.064	1.710	.593

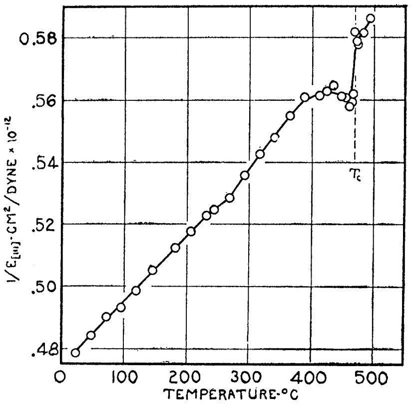

FIG. 3. $1/E_{[111]}$ against temperature.

necessarily contain a large proportion of crystals with orientation function near 0.250. The reciprocal of Young's modulus in the [100] direction, shown in the upper curve of Fig. 2, decreases rapidly. This is very surprising in view of the fact that in almost every other known material just the reverse is true. Insofar as the writer knows, no theories as yet have been proposed which would predict such an abnormal behavior as this. It seems not unlikely that a close connection may exist between the unusual anisotropy exhibited by beta-brass and the peculiar temperature dependence of the elasticity in this temperature region. The different behaviors of these three curves near room temperature suggest that, perhaps, measurements on the material at much lower temperatures might be of some interest. Such an investigation is planned.

Above 150°C, the very rapid increase in slope in $1/E_{[100]}$ $(=s_{11})$ and $1/E_{[110]}$, Fig. 2, is undoubtedly due to the disappearance of order, and is in close agreement with the experimental results of Siegel[5] for Cu_3Au and Köster[7] for polycrystalline beta-brass. Köster found that disordering caused the value of $1/E$ to be about 30 percent higher at 470°C than its value at 150°C, and the writer's results indicate that over the same temperature interval, $1/E_{[110]}$ increases about 37 percent. The behavior of $1/E_{[111]}$, as shown in Fig. 3, is quite different from the behavior of either of the curves in Fig. 2. The linear increase, observed between 25°C and 150°C, is extended right up to 400°C; therefore, disordering presumably produces no particular

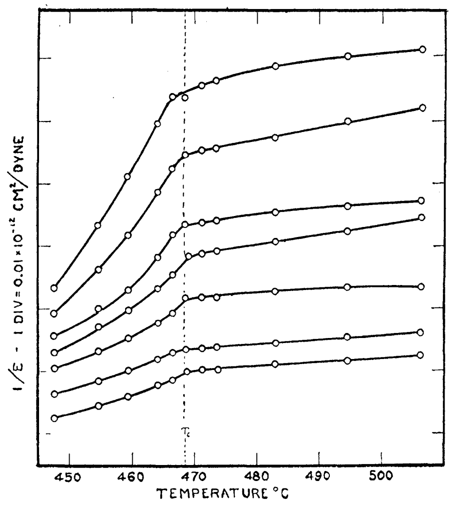

FIG. 4. $1/E$ against temperature for individual crystals in the neighborhood of the critical temperature. Values at critical temperature are, reading from top to bottom (increasing orientation function): 4.686, 3.846, 2.758, 2.433, 1.791, 1.433, and 1.349×10^{-12} cm²/dyne, respectively.

effect in this region. Between 400°C and the critical temperature, 468°C, the curve shows a decided dip with a subsequent sharp rise at the critical temperature. It may be that this dip in the curve is only a result of the computational method used; if, however, it is real, only the last sudden disappearance of order modifies the steady rise of this quantity. In any case the effect of disordering is far less noticeable in this direction than it is in any other direction in the crystal. No crystal oriented exactly in the [111] direction was available, so that the reality of the dip could not be confirmed by a direct, independent run on a crystal.

An abrupt change in slope for each of the three curves in Figs. 2 and 3 occurs between 468°C and 469°C. This is due to the final disappearance of order. There is evidently no discontinuity in the curve such as has been observed in similar curves for Cu_3Au.[5] This is in agreement with the fact that discontinuities in specific heat[17] and resistivity[5] are found for Cu_3Au but not for beta-brass. Webb[4] points out the existence of a fairly well defined "tail" on his resistivity *vs.* temperature curves. In Fig. 4, the reciprocal of Young's modulus against temperature is plotted, on a greatly enlarged scale, in the neighborhood of the critical temperature for each of the seven crystals run. There is no evidence of a tail of width greater than two degrees, which is the maximum difference in temperature between the two ends of the crystal. It is very likely, therefore, that the slope is discontinuous at the critical temperature.

Above the critical temperature, the reciprocal modulus shows the normal behavior, i.e., it increases with temperature for any direction in the crystal lattice. (See curves in Figs. 2, 3, and 4.)

The dependence of critical temperature upon relative concentration of zinc and copper has been measured by Sykes and Wilkinson.[18] They find the critical temperature for the composition used in this investigation to be 468°C. This agrees closely with the value obtained by the writer, which certainly lies somewhere between 468°C and 469°C.

ANISOTROPY AND TEMPERATURE

While the degree of anisotropy of the crystal varies with temperature, as can be seen from the results already cited, it is of some interest to consider it specifically. Taking as before, $E_{[111]}/E_{[100]}$ as a measure of the anisotropy, its variation with temperature is shown, graphically, in Fig. 5. While initially the anisotropy does decrease slightly, it increases again rapidly in the very region where the disordering is proceeding most rapidly. Thus, it appears that the simple argument advanced to support Webb's[15]

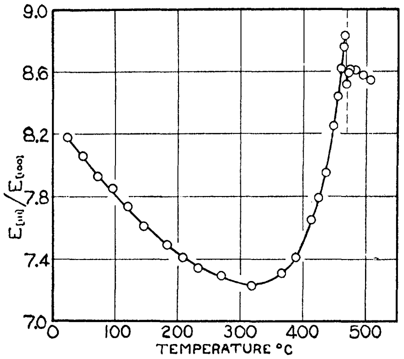

FIG. 5. Anisotropy in Young's modulus against temperature.

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[17] The discontinuity in specific heat is expected on theoretical grounds, reference 1, Section 14.

[18] C. Sykes and H. Wilkinson, J. Inst. Metals **61**, 223 (1937).

hypothesis is entirely too simple a picture. The rapid fluctuation in the curve just at the critical temperature is due to the previously discussed dip in the curve of Fig. 3. The same remarks as to its genuineness would apply. Just beyond the critical temperature, the anisotropy begins to decrease with increasing temperature just as it does in the neighborhood of room temperature. A qualitative picture of the temperature dependence of this anisotropy can be obtained by considering the behavior of the lower line of Fig. 1, as temperature is increased. The curve rotates counterclockwise about the value of $F(l,m,n)$, which corresponds to the [110] direction in the crystal lattice, until the temperature at which disorder begins to set in is reached, i.e., 150°C. As disordering proceeds, the rotation becomes clockwise and, in addition, the whole curve shifts upward until finally at the critical temperature it has risen considerably above its position at room temperature and possesses a much greater slope. Curve A, in Fig. 1, is a plot at a temperature just below the critical temperature, where the anisotropy is a maximum.

In conclusion, the writer gratefully acknowledges his indebtedness to Professor E. P. T. Tyndall for much helpful advice and many valuable suggestions throughout the work; to the Physics Department of the State University of Iowa for the facilities generously placed at his disposal; and to others who assisted him in this work.

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The Internal Friction of Single Metal Crystals*

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The internal friction of crystalline copper, tin, lead, and zinc has been measured by the composite piezoelectric oscillator method. It is found that the decrement of an unannealed crystal may be as large as that of the polycrystalline material, that annealing reduces the decrement to a value of the order 10^{-4} to 10^{-5}, and that both Young's modulus and the decrement vary with the vibrational strain amplitude at strain amplitudes as low as 10^{-6}. In the case of zinc crystals, a detailed study has been made of the way in which the elastic modulus and internal friction depend on the previous history of the specimen, on the vibration frequency and amplitude, and on the orientation of the vibration axis with respect to the crystal slip planes. The results suggest that the mechanism involved is a propagated "dislocation" of the sort proposed by Taylor, Polanyi and Orowan to account for macroscopic plastic flow, and that the application of a stress is accompanied by a plastic strain, together with an associated strain hardening in consequence of which the stress-strain relation on removal of the applied stress is nearly elastic.

INTRODUCTION

INTERNAL friction is a property of matter in virtue of which organized energy of imperfectly elastic stress is rendered irrecoverable, or unavailable for mechanical work. Thus a specimen body which is carried adiabatically through a complete stress cycle can be restored to its initial state only by the removal of a certain amount of heat, and this heat, called the "energy dissipated per cycle," affords a measure of the internal friction.

The "coefficient of internal friction," ξ, of a substance is defined by the formula[1]

$$W^d = \xi S^2, \qquad (1)$$

where W^d is the energy dissipated per cycle per unit volume, and S is the stress amplitude. The internal friction of solid materials is usually studied by observing the behavior of a properly

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[1] A. L. Kimball and D. E. Lovell, Phys. Rev. **30**, 948 (1927).