

A Study of Beta-Brass in Single Crystal Form

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The resistances of twenty single crystals of brass in the beta-phase have been measured as a function of temperature from room temperature to about 550°C for the purpose of studying the order-disorder phenomenon. The results obtained are compared with the theory of Bragg and Williams. The resistivities at 25°C as a function of composition place the limits of the beta-phase at 51.3 and 55.5 atomic percent copper. A study of the thermal e.m.f. of the crystals against copper shows only a slight discontinuity in the second derivative of the e.m.f.-temperature curve at the temperature of complete disorder. The e.m.f. curves themselves are quite smooth. Young's modulus, E , for ten of the crystals, measured at room temperature, gives the elastic constant S_{11} , (44.8×10^{-13} cm²/dyne) and the combination of constants, $2S_{12} + S_{14}$, (0.028×10^{-13} cm²/dyne). A graph of $1/E$ against the orientation function, $(l^2m^2 + m^2n^2 + n^2l^2)$ is linear. From it the ratio of the maximum to minimum E is found to be 8.94. Below the elastic limit the stress-strain relation is linear with no permanent set nor hysteresis.

INTRODUCTION

RESEARCHES on the properties of metal alloys capable of forming superlattices have been stimulated, particularly in this country and England, by the recent theoretical developments of Bragg and Williams,¹ and Bethe.² Improvements in details of the theory have been made by a number of workers.³ On the experimental side specific heat and electrical resistance have been determined as functions of temperature and have been correlated with the state of order existing.⁴ An excellent review of both theory and experiment has been given recently by Nix and Shockley.⁵

Beta-brass is one of the simplest of alloys showing the order-disorder phenomenon. It is the beta-phase of the copper-zinc system, with a composition in the neighborhood of the one-to-one ratio of atoms. The crystal structure is body-centered cubic. In the disordered state the two kinds of atoms have equal probabilities of being at any lattice point. In the ordered condition the zinc atoms occupy the cube centers

and the copper atoms the cube corners or vice versa. This fact, though surmised from other data, was definitely established by Jones and Sykes in an x-ray study in which they were able to obtain superlattice lines for the ordered alloy⁶ by a judicious selection of the x-ray wave-length used.

The present research includes a study of certain properties of single crystals of this beta-brass in the ordered condition (at room temperature), and of the order-disorder transformation by following the changes in certain properties as the temperature is gradually raised to a point above the critical temperature.

PREPARATION OF CRYSTALS AND DETERMINATION OF ORIENTATION

The beta-brass from which the crystals were grown was prepared from very pure commercial materials. The copper was cathode copper from Anaconda Copper Company and was stated by the Company to be 99.95 percent copper. The zinc was Bunker Hill from Platt Brothers and Company and contained not more than 0.01 percent impurity.⁷

¹ W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **A144**, 340 (1934).

² H. A. Bethe, Proc. Roy. Soc. **A150**, 552 (1935).

³ R. Peierls, Proc. Roy. Soc. **A154**, 207 (1936); N. F. Mott, Proc. Phys. Soc. **49**, 258 (1937); T. S. Chang, Proc. Roy. Soc. London **A161**, 546 (1937); E. E. Easthope, Proc. Camb. Phil. Soc. **33**, 502 (1937).

⁴ C. Sykes and F. W. Jones, Proc. Roy. Soc. **A157**, 213 (1936).

⁵ F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938).

⁶ F. W. Jones and C. Sykes, Proc. Roy. Soc. **A161**, 440 (1937).

⁷ An estimate of the impurities present in this brand of zinc is given by H. E. Way, Phys. Rev. **50**, 1181 (1936). Actually the writer's material was all taken from a slab which showed distinctly less lead than Way's, but other impurities in the same amount. See Way's footnote 14, which refers to the slab used by the writer.

The crystals were grown from the molten state in a horizontal mold by the method employed for some time in this laboratory.⁸ The preliminary polycrystalline casting was prepared by melting together in a crucible⁹ suitable proportions of copper and zinc and pouring the molten metal into the crystal mold. This was done in a furnace in which a nitrogen atmosphere was maintained throughout. The crystal was grown in a second furnace also in nitrogen. The orientation of the crystal was not predetermined by the use of a nuclear crystal, since it was found that, by making the end of the casting pointed, a single crystal would start. There seemed to be no particularly preferred orientation, so that thus a suitable variety of orientations was assured.¹⁰ The crystals were of a trapezoidal (nearly square) cross section, about 0.7 cm² in area, and 14 cm long. All the crystals were grown with a temperature gradient of about 6°C/cm and a rate of growth of approximately 6 cm/hr.

During the cooling following the formation of the crystals the temperature was checked at 600°C for twenty-four hours and then allowed to fall slowly to room temperature. The purpose of this anneal was to secure homogeneity of composition throughout the crystal.

After completion of the measurements the crystals were analyzed for copper content by the

standard method of electrolytic deposition from a sulfate solution. In most cases the sample analyzed was about 3 g, 1.5 g from each end of the crystal. In three cases separate analyses were also made for the two ends. None of these showed a difference between the two ends greater than 0.1 percent of copper content. The compositions obtained extended throughout the beta-brass phase and somewhat beyond at room temperature as can be seen from Table II.

The crystals, as removed from the mold and without further treatment, showed in a very marked manner the phenomenon of strong light reflection in definite directions, precisely as described by Bridgman¹¹ for a number of metal crystals. These reflections could be improved in some cases by heating the crystals from two to three hours in a hydrogen atmosphere. Etching the surfaces damaged the reflections and made them more diffuse.

These reflections were used to determine the orientation of the length of the specimen relative to the space lattice by a slight variation of Bridgman's method. The general idea of the method is to locate the normal to each reflecting plane by causing a fixed beam of incident light to be reflected back on itself. When the normals to a number of planes have been located, the angles between the planes are then easily computed. To identify the planes it is then necessary to see whether each plane can be assigned a set of Miller indices so that measured and computed angles between every possible combination of pairs of planes form a completely consistent scheme. Table I shows the degree of consistency

⁸ C. A. Cinnamon, *Rev. Sci. Inst.* **5**, 187 (1934).

⁹ The crucible and molds were made from lava obtained from the American Lava Company. The writer is indebted to the company for furnishing the unfired material and later firing the molds, etc., after they were made.

¹⁰ It is doubtful if a seed crystal could be fused to the casting with a flame since attempts to fuse two pieces of beta-brass together resulted in evaporating so much zinc that the joint became alpha-brass.

¹¹ P. W. Bridgman, *Proc. Am. Acad. Arts and Sci.* **60**, 305 (1925).

TABLE I. Orientation of crystal lattice, measured angles.

1	2	3	4	5	6	7	8		REFLECTED BEAM NO.
{111}	{110}	{110}	{111}	{110}	{111}	{110}	{110}	ASSUMED PLANE	
	35° 8'	35° 25'	70° 45'	89° 59'	70° 26'	89° 53'	89° 50'	{111}	1
		60° 3'	35° 36'	59° 44'	89° 52'	58° 54'	89° 35'	{110}	2
			89° 54'	60° 16'	35° 7'	89° 59'	60° 3'	{110}	3
				34° 56'	70° 19'	35° 7'	89° 56'	{111}	4
theoretical angles					35° 25'	59° 41'	60° 11'	{110}	5
{111} with {111} 0°, 70° 32'						89° 58'	35° 36'	{111}	6
{111} with {110} 35° 16', 90°							60° 9'	{110}	7
{110} with {110} 0°, 60°, 90°.								{110}	8

obtained for eight of the reflections from one of the crystals. The numbers across the top and down the side refer to arbitrary numbers assigned to the reflections. In parentheses are the Miller indices which give the type of plane. The angles in the body of the table are those observed between the normals to the planes in the corresponding column and row. It can be seen that rarely do the observed angles disagree by more than one degree with one of the geometrically possible angles given in the table. More complete tables involving all observed reflections, were fully as consistent. Besides the two types of planes shown in the table, planes of type {112} were frequently observed.

The above measurements were made by use of an especially constructed goniometer, which need not be described in detail. It permitted one to obtain a particular reflection from the whole of the crystal length without disturbing the angle setting. Only specimens for which the direction of the reflection remained constant the full length were considered to be single crystals and satisfactory for use in subsequent measurements.

Naturally, once the positions and types of several lattice planes are determined, it is merely a matter of geometry to compute the orientation. The orientations so obtained are given in Table II by stating the two larger of the three direction cosines of the long axis of the specimen with reference to the three principal crystal axes (cube edges). While it has been stated that the angles between the lattice planes did not involve an error greater than one degree the error involved in the orientation angles may be as great as three degrees. This difference is caused by inability to set the specimen in a precise manner on the goniometer.

RESISTIVITY AND RESISTANCE

Two sets of resistance measurements were made on each crystal; one to obtain an accurate value of the resistivity at room temperature, and the other to study the temperature dependence of resistance. A potentiometer method employing a Leeds & Northrup, Type K2, potentiometer was used to make both sets of measurements.

For the resistivity measurements needle points were used as potential contacts which made

TABLE II. Resistance characteristics of the crystals. Limits of the beta-phase are indicated by the arrows. T' and T'' represent the temperatures between which the resistance-temperature curves were nonlinear.

ATOMIC PERCENT COPPER	$\alpha \times 10^8$ PER °C	$\rho''' - \rho''$ $\times 10^6$ OHM-CM	T' (°C)	T'' (°C)	TWO LARGEST DIRECTION COSINES	
					l	m
50.22	3.54	4.40	193	490	0.806	0.560
50.70	3.85	4.31	250	480	.807	.562
50.81	3.47	4.41	200	490	.622	.561
50.89	3.41	4.37	165	485	.868	.396
51.25	3.61	4.46	207	490	.914	.294
51.63	3.50	3.62	240	480	.693	.656
52.13	3.43	3.76	250	475	.986	.097
52.16	3.53	4.03	205	487	.908	.357
53.20	3.02	3.76	160	475	.788	.488
53.34	3.32	4.35	160	485	.876	.439
53.65	2.96	3.46	175	490	.914	.334
53.77	3.16	3.04	185	490	.801	.435
53.81	2.42	4.30	150	480	.813	.583
54.25	2.87	2.68	212	480	.717	.633
54.26	3.07	3.09	210	480	.716	.716
54.60	3.12	2.57	240	465	.739	.584
54.89	3.08	3.34	150	475	.900	.453
55.50	2.96	2.99	200	485	.779	.624
55.85	3.00	2.67	200	490	.933	.291

possible a precise measurement of the length. The average cross-sectional area between the potential contacts was determined by finding the volume of this portion of the crystal. This was done by sawing out this section, at the completion of the work, and getting its mass and density.

To measure the resistance as a function of temperature the crystal was placed in a furnace in a holder equipped with three thermocouples, one near the middle and one near each end of the crystal. The potential and current leads were spot-welded to the crystal. Readings were taken as the temperature of the furnace was raised at a rate which varied from a degree per minute for the lower temperature range to about one-fourth degree per minute at the higher temperatures.¹² Readings were also taken with the temperature decreasing gradually to 400°C, and a final reading at room temperature. There was a slight temperature gradient along the crystal of such

¹² These runs were made at this slow rate to eliminate any lag between the temperature indicated by the thermocouples and the actual temperature of the crystal. The agreement for rising and falling temperatures shows that this was accomplished. It shows further no lag between order and temperature; such a lag was not expected, however, since it is known that the relaxation time for this alloy is very short.

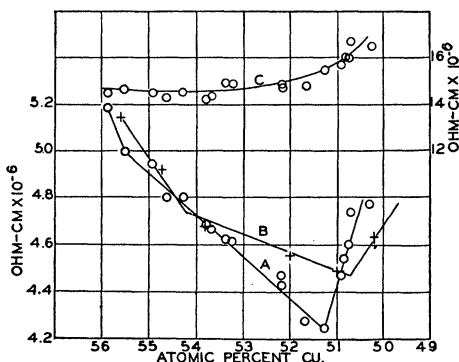


FIG. 1. Resistivity as a function of composition. Curve A at 25°C; curve C at 500°C. Curve B, Haughton and Griffiths' curve; they state their values are for room temperature. The ordinate scale for C is on the right.

amount that the temperatures at the potential contacts usually differed by about three degrees, never, however, exceeding ten degrees. Thermal e.m.f.'s caused by this difference were corrected for by taking potential readings with the current through the crystal both direct and reversed; also, with no current.

In curve A, Fig. 1, the resistivity at 25°C is shown as a function of composition. Curve B, given for comparison, represents the data of Haughton and Griffiths¹³ for polycrystalline material at "room temperature." The two curves are seen to agree in a general way. Some of the difference is undoubtedly caused by difference in purity of materials and to the mechanical treatment given the samples of Haughton and Griffiths.

The boundaries of the beta-phase occur at the end points of the middle straight section of the resistivity-composition curve. The writer's data (curve A) indicate 51.3 and 55.5¹⁴ atomic percent copper whereas Haughton and Griffiths estimate 50.7 and 54.2 atomic percent copper from their data. Values given by metallurgists, obtained usually by thermal and micrographic analyses, vary considerably among themselves. The exact limits of the beta-phase at room temperature are extremely difficult to determine, since, while an alloy may be examined at room

¹³ J. S. Haughton and W. T. Griffiths, *J. Inst. Met.* **34**, 245 (1925).

¹⁴ This boundary is not closely established by the data. The break in the curve might well come anywhere between 54.5 and 55.5 percent Cu with an equally good fit of the curve to the observed points.

temperature, the structure observed may be typical of a higher temperature if the cooling to room temperature has been too fast, or perhaps at any finite rate. Some typical values for the beta-phase limits in atomic percent copper are: Gayler:¹⁵ 55.0–51.0; Hansen:¹⁶ 55.6–51.0; Saldau and Schmidt:¹⁷ 54.4–49.8; *International Critical Tables*: 54.7–51.2. Sykes and Wilkinson¹⁸ obtained phase boundaries by measurement of the energy difference of the ordered and disordered state as a function of composition. Their limits are: 55.3 and 51.1 atomic percent copper, in very good agreement with the writer's.

It is interesting to note that practically all determinations of the beta-phase of brass just fail to include the ideal, equiatomic ratio. It is only for such a ratio that perfect order, or a perfect superlattice can exist. Other compositions in the beta-phase may have a maximum order, but never perfect order since the number of copper atoms is always too large. Sykes and Wilkinson in order to find the transformation energy for the ideal CuZn, extrapolated their data to the one-to-one ratio. The writer's resistivity data may be treated in the same way by extending the straight middle portion of curve A, Fig. 1, to 50 atomic percent copper. The value of the resistivity so found is 4.02×10^{-6} ohm-cm. This is very near the mean value of the resistivities of the constituent metals, which is 3.93×10^{-6} , derived from Way's¹⁹ value for Bunker Hill zinc, and the *International Critical Tables* value for pure copper. This shows that the completely ordered structure behaves in resistivity like a pure metal, with value intermediate between those of the constituents, and does not show the enhanced resistivity characteristics of an ordinary, or random, solid solution. The temperature coefficient, as will be seen later, is also about that of a pure metal. This simple relation seems to be approximately satis-

¹⁵ M. L. V. Gayler, *J. Inst. Met.* **34**, 235 (1925).

¹⁶ M. Hansen, *Der Aufbau der Zweistofflegierungen* (Julius Springer, Berlin, 1936).

¹⁷ P. Saldau and I. Schmidt, *J. Inst. Met.* **34**, 258 (1925). The specimens of Saldau and Schmidt were annealed 84 days at 440°C.

¹⁸ C. Sykes and H. Wilkinson, *J. Inst. Met.* **61**, 223 (1937). These authors give a good discussion of the uncertainties of these boundaries.

¹⁹ Reference 10. An average value for random orientation is given by $\frac{2}{3}\rho_{90}$ and $\frac{1}{3}\rho_0$. The value so obtained is reduced to 25°C, and gives the value in the text.

fied in other similar cases²⁰ but in this case is really surprising in view of the very different lattice structures of the alloy and either constituent (alloy, b.c.c.; copper, f.c.c.; and zinc, hex.).

Curve C of Fig. 1 gives the resistivity at 500°C. These data are taken from the resistivity at room temperature combined with the resistance temperature results, to be described later. It is seen that the phase boundaries are no longer defined by this curve. All the crystals were within the beta-phase at this temperature. This curve is similar to those for continuous solid solutions, such as shown by Mott and Jones.²¹

The very regular variation of the resistivity with composition shown by curves A and C, Fig. 1, indicates that there is certainly no very large dependence of resistivity on orientation. In view of the fact that the lattice structure is cubic it is almost certain that no such variation should be expected.

The curves of Fig. 2 show typical resistivity-temperature relations. Both curves are for crystals inside the β -phase, one, A, near the boundary on the copper rich side, and one, B, near the other boundary and very close to the ideal equiatomic ratio. These curves have the following features: a straight portion at lower temperatures followed by a portion of rapidly increasing slope, a short "tail" of decreasing slope, and finally another linear portion extending to higher temperatures. The curves for all the other crystals were similar to these two. Without presenting all these curves, the differences between crystals may be indicated as follows. If the straight line portions are extended (curve B), the point T' at which the curve departs from the lower tangent marks the onset of detectable disorder, while T'' marks the completion of the principal disordering process. Furthermore, the difference, $\rho''' - \rho''$, is the contribution of disorder to the resistivity under the assumption that the temperature dependence of resistivity, aside from disorder, may be

linearly extrapolated. Values for such quantities taken from corresponding curves for all the crystals are given in Table II. This table includes also the composition and temperature coefficient of resistivity of the ordered state taken from the resistance-temperature curves.

It is seen from this table that the total contribution of the disorder to the resistivity is roughly greater the closer the crystals are to the ideal equiatomic ratio. There are, however, easily noted exceptions to this general behavior. These arise largely because of the irregularity of occurrence of the temperature T' , which is seen to range from 150° to 250°C. When it comes at a high temperature, less resistance change is attributed to disorder, than when it comes low. However, for want of a better criterion it seems fair to consider the "disordering" as starting in a noticeable fashion at T' as chosen. The general trend to lower values of $\rho''' - \rho''$ for increasing copper content seems reasonable because the greater the excess of copper (above equiatomic proportions) the less the completeness of the order which must be destroyed at the high temperature. The alloys beyond the beta-phase, at the top and bottom of the table, behave quite similarly to alloys just within. These alloys in the two-phase field are quite interesting in that the disordering process is accompanied by change of the alpha- or gamma-brass present to the

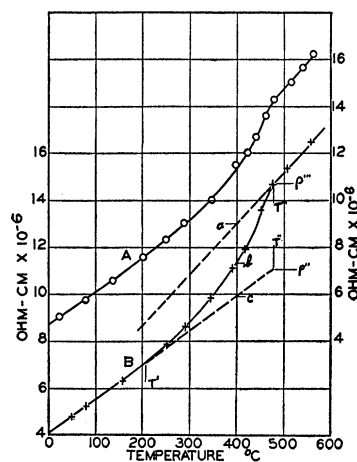


FIG. 2. Resistivity-temperature. Curve A for crystal of 55.50 atomic percent copper. Curve B for one of 51.25 atomic percent copper. The ordinate scale for curve A is on the right.

²⁰ See F. C. Nix and W. Shockley for CuAu and CuPd systems.

²¹ N. F. Mott and F. W. Jones, *The Theory of Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), Fig. 103, page 299 and Fig. 104, page 300.

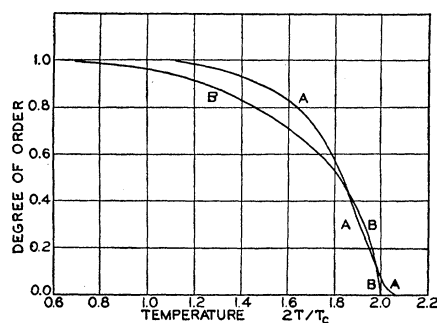


FIG. 3. Order versus temperature. Curve A, experimental curve for crystal 51.25 atomic percent copper. Curve B, Bragg-Williams theoretical curve for equiatomic ratio.

beta-phase as the resistance-temperature measurements are made.

The completion of disorder is far more definite than the onset, as shown by the smaller range of values of T'' , 475°C to 500°C. The existence of the "tail" at the upper portion of the curves is quite definite and was shown by all the crystals. Points on it could be repeated on different runs, on the same run for heating and cooling, as well as by holding a constant temperature at a particular point. Only a small part of this "tail" is caused by the slight temperature gradient along the crystal since the width due to this cause should not exceed the difference in temperature between the points of contact, which was in most instances certainly less than 5°C with an observed "tail" of the order of 15°C wide. Thus in no case was there any indication of a discontinuity at the critical temperature in the slope of the resistivity-temperature curve such as is indicated for Cu_3Au by Sykes and Jones⁴ and by Kurnakow and Ageew.²² As far as the writer can tell from the figures published by Haughton and Griffiths²³ for a single polycrystalline specimen of brass containing 47 percent copper by weight, no pronounced "tail" is present, but on the other hand, there is no indication of the very sudden upturn of the resistance-temperature curve and the consequently very marked discontinuity just mentioned.

The temperature coefficient of resistivity of the ordered state is seen likewise to decrease in

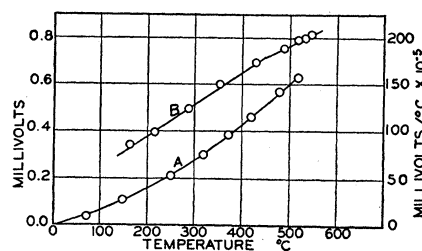


FIG. 4. Curve A, ordinate scale on left, shows a typical thermal e.m.f.-temperature relation. Curve B, ordinate scale on right, thermoelectric power-temperature.

general as the composition varies from the neighborhood of the equiatomic ratio toward the copper-rich side of the phase. This is to be expected because the behavior should depart from that of an ordered alloy and approach that of a disordered solid solution. From the curves of Fig. 2 it is seen that the slopes of the upper linear portions are greater than those of the lower. This tendency was general, the difference in the slopes being greater the greater the copper content of the crystals. There seems to be no obvious explanation for this unless perhaps it be attributed to a gradual disappearance of local order after the main disordering process is complete.

A very rough estimate of the dependence of resistivity on order has been made by Bragg and Williams.¹ They assumed essentially that the amount of added resistance was proportional to the disorder present. This may be illustrated from curve B of Fig. 2 in which the order at any temperature is given by the ratio of the ordinate segments, ab/ac . Curve A, Fig. 3, is a plot of the order obtained in this way, for the crystal of 51.25 atomic percent copper. For abscissae a reduced temperature, $2T/T_c$, is used, in which T is the absolute temperature and T_c is the critical temperature at which long range order disappears. As the critical temperature for this composition the writer has adopted the carefully determined value of Sykes and Wilkinson,¹⁸ 741°K (468°C). For comparison the Bragg and Williams¹ curve for long range order and for equiatomic proportions is shown, curve B, Fig. 3. The general agreement is fairly good. The assumption that has been made throughout that order is complete at room temperature naturally causes the experimental curve to lie above the

²² N. S. Kurnakow and N. W. Ageew, *J. Inst. Met.* **46**, 481 (1931).

²³ Reference 13, Figs. 2 and 3, pp. 248-249.

Bragg and Williams curve in the high order region.²⁴ The order shown beyond the critical temperature is largely due to the "tail" of the resistance-temperature curves, a possible explanation for which has already been suggested. Similar curves for the other crystals are somewhat as follows: (1) crystals near the equiatomic ratio agree very well with curve A; (2) crystals of high copper content differ from curve A, and lie about ten percent or less above or below it in regions of order greater than 0.5, and distinctly to the right in the region of rapidly decreasing order, below 0.5; (3) crystals with copper less than the equiatomic proportion lie very close to curve A for high order and either close or slightly to the left in the region of lower order.

The theory of T. Muto²⁵ leads to a connection between order and resistivity given by:

$$\rho = \rho_1 + \rho_2 S + \rho_3 S^2.$$

A comparison of the above experimental results with this expression is not possible because of the inability to evaluate the quantities ρ_1 , ρ_2 and ρ_3 which are themselves temperature dependent. The Bragg and Williams approximation is equivalent to the first two terms of Muto's expression.

THERMAL e.m.f. AND THERMOELECTRIC POWER

The thermal e.m.f. of the crystals against copper was measured from room temperature up

TABLE III. Elastic characteristics of the crystals.

$f(l, m, n)$	$E \times 10^{-11}$ (DYNES/CM ²)	$1/E \times 10^{13}$ (CM ² /DYNES)	ATOMIC PERCENT Cu
0.143	3.62	27.6	53.65
.183	4.02	24.9	53.34
.243	6.07	16.5	55.50
.009	2.29	43.8	52.13
.193	5.39	18.7	50.89
.286	8.25	12.1	54.60
.231	6.00	16.6	50.22
.323	14.3	6.97	50.81
.162	4.18	24.1	52.16
.145	4.62	21.6	51.25

²⁴ This deviation could be lessened if the Bragg and Williams procedure had been exactly followed. Thus, instead of using the experimental resistivity near room temperature as typical of the completely ordered state, an ideal resistivity would have been used, namely, the average resistivity of copper and zinc.

²⁵ T. Muto, Sci. Pap. Inst. Phys. Chem. Res. 30, 99 (1936).

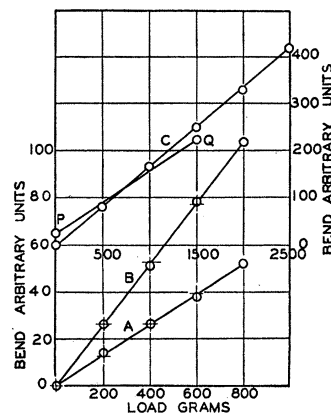


FIG. 5. Curves A and B, ordinate scale left, show load-strain relationship. Curves C and PQ, ordinate scale right, show the effect of plastic flow.

to 550°C. The curves obtained for e.m.f.-temperature difference were quite smooth, with no noticeable effect in the region of disordering. A typical result is given in Fig. 4, curve A. The e.m.f. values for all the crystals ranged from 0.4 to 0.7 millivolt for a hot junction temperature of 500°C and cold junction at 18°C. The variation from crystal to crystal did not correlate with the composition nor orientation of the crystals. The mean thermoelectric power in a 15° temperature interval was directly measured for six of the crystals. When plotted against temperature it shows two straight line portions intersecting at 460°±15°C with the higher temperature part having the smaller slope. Curve B, Fig. 4 is typical. Although these thermoelectric investigations were not very extensive they show conclusively that the degree of order affects the thermoelectric properties very slightly. The only effect is a slight change in the second derivative of the thermal e.m.f.-temperature relation, which occurs apparently very close to the temperature of completion of disorder.

ELASTIC BEHAVIOR

Ten of the crystals with the most uniform and regular cross section were selected for a preliminary study of their elastic behavior. Young's modulus was measured for each crystal on the bending beam apparatus described by Hanson.²⁶

²⁶ The apparatus has been somewhat modified by Professor Tyndall. An improved and more sensitive optical system for observing the bending is now in use. Further-

Two typical stress-strain curves are shown in Fig. 5, A and B. The curves were all taken with increasing load (circles) followed by decreasing load (crosses). It will be seen that there is no sign of hysteresis nor permanent set. In these curves the maximum load reading corresponds to a tensile stress on the top surface of the beam of about 20×10^6 dynes/cm². The values for Young's modulus for the ten crystals are given in Table III.

The limit of proportionality between stress and strain and the beginning of plastic flow were obtained for one crystal. The crystal was first taken up to a load of 2500 g and on unloading it returned to zero. (See Fig. 5, curve C.) It was then again loaded to 2500 g, and the preceding readings were duplicated. An additional 500 g caused a rapid drift (plastic flow). The whole load was immediately removed,²⁷ and the crystal returned to a new zero as shown by the point marked P. A 1500-g load then gave the point Q. When this was removed point P was again obtained. From these results it seems clear that the limit of proportionality and the beginning of plastic flow are very close together, if not identical. The increase in the modulus (about 20 percent) shown by the decreased slope of PQ is very marked after such a small permanent deformation. The tensile stress on the upper surface of the beam for the 2500-g load is 70×10^6 dynes/cm². The strain is 1.4×10^{-4} . A second crystal (50.05 atomic percent copper) was strained until the maximum tensile stress on the upper surface of the beam was 80×10^6 dynes/cm² without, however, exceeding the proportional limit. The "yield point" determined by Elam²⁸ for beta-brass is of the order of 10 times the above values. This difference is not surprising in view of the fact that Elam's values are for permanent extensions sufficient to cause slip bands to appear. The extreme values of tensile

more, a cylindrical roller on a flat block is used in place of one of the knife edges, since it was found that with two knife edges a frictional drag occurred. This was undoubtedly the cause of the small hysteresis observed by Hanson. The fact that no such hysteresis exists for zinc crystals when the roller is used is now definitely established. Van Allen also obtained no hysteresis when measuring Young's modulus for a zinc crystal by a direct stretch method (Thesis, State University of Iowa, 1936).

²⁷ The extra 500 g was acting at the most, for 10 seconds.

²⁸ C. F. Elam, Proc. Roy. Soc. A153, 273 (1935-36).

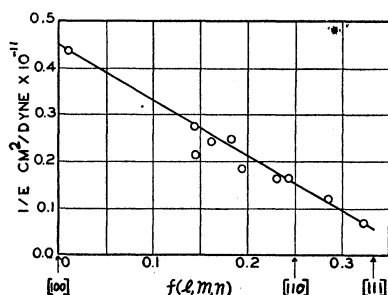


FIG. 6. Reciprocal of Young's modulus, $1/E$, versus $f(l, m, n) = (l^2m^2 + m^2n^2 + n^2l^2)$. The arrows at the bottom show directions in the lattice that correspond to certain values of $f(l, m, n)$.

stress obtained by the writer would correspond to a resolved shear stress of about 35×10^6 dynes/cm², i.e., half the tensile stress provided a slip plane²⁹ is near the most favorable orientation of 45° to the length of the specimen.

For a cubic crystal Young's modulus in a given direction may be expressed in terms of the elastic parameters, S_{11} , S_{12} and S_{44} and the direction cosines, l , m and n , as follows:

$$1/E = S_{11} - (2S_{11} - 2S_{12} - S_{44}) \times (l^2m^2 + m^2n^2 + n^2l^2), \quad (1)^{30}$$

where $(l^2m^2 + m^2n^2 + n^2l^2)$ is called the orientation function, $f(l, m, n)$. Since $1/E$ is linear in $f(l, m, n)$, a straight line should result when the reciprocals of the values obtained for Young's modulus are plotted against $f(l, m, n)$. Fig. 6 is such a plot for the values given in Table III. The points, with the exception of two,³¹ lie within experimental error on a straight line. This is true in spite of the fact that these crystals differ widely in composition, some even being outside the beta-phase. The value of S_{11} , the intercept on the $1/E$ axis ($f=0$), is 0.448×10^{11} cm²/dyne. This corresponds to a Young's modulus of 2.23×10^{11} dynes/cm² in the $[100]$ direction, in which direction the modulus is a minimum. The maximum value of the modulus obtained from the reciprocal of the ordinate at $f(l, m, n) = \frac{1}{3}$

²⁹ Slip planes are not definitely known for beta-brass. The glide direction is probably $[111]$ according to Elam and the slip plane possibly (110) or (112) .

³⁰ E. Schmid and W. Boas, *Struktur und Eigenschaften der Materie XVII, Kristallplastizität*.

³¹ The discrepancies for these two points are definitely greater than can be attributed to experimental error. The writer is unable to account for them.

is 19.9×10^{11} dynes/cm². This is for the [111] direction, or space diagonal. The modulus at $f=0.25$ includes among other possible directions, the face diagonal [110]. This value is 6.54×10^{11} dynes/cm². The material shows an unusually high degree of elastic anisotropy as may be seen from the large value, 8.94, of the ratio of the maximum to the minimum modulus in comparison with other metal crystals. For instance some metals of face-centered cubic structure have values of this ratio: Al 1.20; Cu 2.85; Au 2.72; Ag 2.64; alpha-brass 3.41. For body-centered cubic alpha-iron the ratio is 2.15 while tungsten (also b.c.c.) is practically isotropic.³² Zinc, which is hexagonal, has a ratio of 3.6.³³ That there is no simple connection between the degree of anisotropy and the particular type of cubic lattice, is perhaps not surprising because of the fact that the elastic behavior does not depend primarily on the geometry of the structure, but on the electrostatic energy of the valence electrons and ions, plus an exchange energy caused by overlapping of ions.³⁴

The slope of the line of Fig. 6 is obviously, from Eq. (1), equal to the combination $-(2S_{11} - 2S_{12} - S_{44})$. From this slope and the value of S_{11} the value of the quantity $(2S_{12} + S_{44})$ may be computed. It is 0.28×10^{-13} cm²/dyne. The

³² Values of cubic metals from tables in E. Schmid and W. Boas: *Kristallplastizität*, pp. 200-202.

³³ This is the ratio of $E_{90}/E_0 = S_{11}/S_{33}$, E. P. T. Tyndall, *Phys. Rev.* **47**, 398 (1935). The max./min. ratio is slightly larger.

³⁴ Reference 20, Chapter IV.

two constants S_{12} and S_{44} cannot be found separately from measurements of Young's modulus alone.

Although this determination of the elastic parameters is not complete and cannot be regarded as of high precision chiefly because of the lack of sufficiently uniform dimensions of the crystals, it is so far as the writer knows, the first attempt to study the elastic behavior of single crystals of this alloy. In spite of the disabilities mentioned, the type of stress-strain relation is clearly shown. The small (or no) dependence of the elastic parameters on the composition is very remarkable particularly when it is remembered that crystals distinctly outside the beta-phase fall in line with the others. The very large anisotropy of Young's modulus with direction of the lattice is a particularly interesting feature. It seems very likely that this is largely because of the high degree of order and that it might become considerably less above the critical temperature.

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