In ferromagnetic metals such as Ni and Fe, on the other hand, the presence of small amounts of impurities can play a dominating role in determining the total thermal expansion for certain temperature regions. This is clearly indicated for the case of Fe by a comparison of our results with those of Austin and Pierce[30] and of Esser and Eusterbrock,[16] as well as results obtained by these workers on irons of slightly different purity. For the temperature region between room temperature and the temperature of liquid nitrogen the role played by small amounts of impurities in Fe is much smaller than in the high temperature region, as evidenced by the rather good agreement between our results and those of Adenstedt[8] and also the older results of Dorsey.[10] Williams[24] demonstrated rather clearly the influence of small amounts of impurities on the thermal expansion for the case of nickel near the Curie temperature.

ACKNOWLEDGMENT

We wish to thank Dr. L. A. MacColl for many helpful discussions of the Grueneisen theory and Dr. K. K. Darrow for his comments in the preparation of the manuscript.

OCTOBER 15, 1941 PHYSICAL REVIEW VOLUME 60

Rigidity Modulus of Beta-Brass Single Crystals

WALTER A. GOOD
Department of Physics, State University of Iowa, Iowa City, Iowa

(Received August 5, 1941)

The rigidity modulus of ten beta-brass single crystals has been measured as a function of crystal orientation and of temperature from 25° to 500°C by the method of the composite piezoelectric oscillator. The reciprocal of the rigidity modulus, $1/G'$, is linearly related to the orientation function. When these data are combined with Rinehart's previous measurements of Young's modulus, the principal elastic parameters are found to be 3.88, -1.52 and 0.578×10^{-12} cm^2/dyne, respectively, at room temperature. Curves and tables give them as functions of temperature up to and slightly beyond the critical temperature for order-disorder. At room temperature, the rigidity modulus is a maximum in the [100] direction, $G'_{[100]}=17.3\times 10^{11}$ dyne/cm^2, and a minimum in the [111] direction, $G'[111]=1.35\times 10^{11}$ dyne/cm^2, and at the critical temperature, $G'[100]=13.5\times 10^{11}$ dyne/cm^2 and $G'[111]=1.06\times 10^{11}$ dyne/cm^2. The elastic anisotropy as given by $G'[100]/G'[111]$ is 12.8 at room temperature, decreases to 12.3 at 250°C and has a value of 13.0 at the critical temperature. The bending-torsion effect was found to be large and in agreement with theory.

INTRODUCTION

THE transition from "order" to "disorder" in certain binary alloys has been studied in terms of changes in various physical properties during this transition.[1] The study of the elasticity of single crystals has been particularly interesting, although a complete theoretical treatment has not been given. Siegel[2] has determined all the principal elastic constants (and corresponding elastic parameters) for Cu_3Au single crystals, from room temperature up to and beyond the critical temperature for order-disorder. Both Webb[3] and Rinehart[4] have worked with single crystals of beta-brass. The former's work included a preliminary study of Young's modulus at room temperature and as a function of the orientation of the crystals. A static method was used. Rinehart, using a more accurate dynamic method extended the work on Young's modulus from about $-80°$ to 500°C (about 30° above the critical temperature). The dependence on orientation was very precisely determined. Rinehart's data established, throughout the temperature range, the elastic parameter, s_{11}, and a

---

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

[2] S. Siegel, Phys. Rev. **57**, 537 (1940).

[3] W. Webb, Phys. Rev. **55**, 297 (1939).

[4] J. Rinehart, Phys. Rev. **58**, 385 (1940) and **59**, 308 (1941).

relation between the other two, s_{12} and s_{44}. The parameters s_{12} and s_{44} cannot be determined separately from Young's modulus alone. In order to get these, some other type of elastic measurement must be made. For the present investigation the measurement of rigidity modulus was chosen. It was measured for a set of ten crystals of various orientations and in a temperature interval from 25° to 500°C. When these data are combined with Rinehart's, there results a complete determination of the three principal elastic parameters throughout the temperature interval.

Whether ordered or disordered the beta-brass[5] crystal structure is body-centered cubic. In the ordered state the copper atoms occupy the corners of the cubes and the zinc atoms the centers. In the disordered state the copper and zinc atoms have equal probabilities of appearing in either the corner or center lattice positions as evidenced by x-ray experiments.[6]

Preparation of Crystals

The crystal specimens were prepared from some of the same material[7] which was used by Rinehart. The crystal growing procedure differed from Rinehart's in two details. Dental casting investment[8] was used instead of Insalute cement to form the mold, and a steel tube leading to the top of the mold allowed the introduction of air or nitrogen under pressure. This prevented pits from forming in the freezing crystal. The crystals produced in this way were smooth and uniform. The rate of lowering of the specimen through the furnace was 3.5 cm/hr. and the temperature gradient was about 20°C/cm. The crystals were four mm in diameter and were grown up to lengths of six cm.

The orientation function, $F(l, m, n)$, of the single crystal specimen is:

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

in which l, m and n are the direction cosines of the specimen length with respect to the three crystallographic axes. These direction cosines were determined as described by Webb[3] and Rinehart.[4] The orientation function may have a value from zero to one-third. The zero value corresponds to a direction along a crystal cube edge, and the one-third value, along a cube diagonal. The direction of the face diagonal has the function equal to one-fourth, but certain other directions also have this value.

Measurement of Rigidity Modulus

The rigidity modulus was measured by the dynamic method of the composite piezoelectric oscillator as used by Siegel[2] and others.[9] The cylindrical brass specimen was cemented to a quartz cylinder of the same diameter. The axis of the latter cylinder coincided with the quartz x axis. Torsional oscillations were excited by applying alternating potentials to four suitably placed electrodes on the quartz crystal. The method finally allows the determination of certain resonance frequencies of the specimen.

The rigidity modulus, G^*, of the specimen at temperature T is given by the formula,[5,10]

$$G^* = 4\rho_{25}L^2{}_{25}f^2(L_{25}/L_T), \qquad (2)$$

in which ρ_{25} is the density at 25°C, L_T the length at T°C, and f is the fundamental resonance frequency of the specimen. The thermal expansion factor L_{25}/L_T, has a value near unity and is calculated from the data of Merica and Schad.[11] Rinehart's value of the density, 8.35 g per cm^3 was used.

The application of an external twisting moment to a crystalline specimen of arbitrary orientation causes bending moments in it.[12] The specific twist (twist per unit length) is different depending on whether flexure is free to occur or is prevented. Thus, in the torsion of a crystal there may exist two measured or effective rigidity moduli. One modulus ($G^* = G'$) results when both twisting and bending are allowed. The other modulus ($G^* = G$) occurs when the bending is prevented. In the case of the cubic crystal the

---

[5] Approximately one-half copper and one-half zinc.

[6] F. Jones and C. Sykes, Proc. Roy. Soc. **161**, 440 (1937).

[7] Kindly supplied by the American Brass Company, Waterbury, Connecticut. Composition was 52.8 and 47.2 atomic percents copper and zinc, respectively.

[8] Ransom and Randolph Gray Casting Investment.

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

[10] This is taken as the definition of G^*. It is, under certain circumstances (see later), either one or the other of two otherwise defined rigidity moduli. Naturally for an isotropic material, G^* is the single rigidity modulus.

[11] P. Merica and L. Schad, Bull. Bur. Stand. **14**, 571 (1918).

[12] W. F. Brown, Phys. Rev. **58**, 998 (1940).

first modulus G', is related rather simply to the principal elastic parameters (s_{11}, s_{12}, s_{44}) and F, the orientation function:

$$\frac{1}{G'}=s_{44}+4sF, \tag{3}$$

where

$$s=s_{11}-s_{12}-\tfrac{1}{2}s_{44}.$$

A less simple formula holds for the other modulus, G:

$$\frac{1}{G}=s_{44}+4sF-\frac{2s^2[F-4F^2+3\chi]}{s_{11}-2sF}, \tag{4}$$

where

$$\chi=l^2m^2n^2.$$

Formula (4) is seen to be the same as (3) except for its last term, the so-called bending-torsion correction.[13] A combination of (3) and (4) gives:

$$\frac{1}{G'}=\frac{1}{G}+\frac{2s^2[F-4F^2+3\chi]}{s_{11}-2sF}, \tag{5}$$

which shows that $1/G'$ is $1/G$ plus the bending-torsion correction. The bending-torsion correction vanishes for certain directions, [100], [110] and [111] in the crystal and hence in these directions G and G' are identical. Some previous work[14] has been done with specimens of only these orientations. The interpretation of such data does not involve the bending-torsion effect.

Measurements have been made, in this and previous investigations[2, 15] on crystals of other than these special orientations. The question has naturally arisen whether G, G', or perhaps neither, has actually been measured. It has been found previously, and here also, that assuming that G is measured gives more consistent and satisfying results. Recently Brown[12] in a theoretical treatment, has given the explanation. According to him, it is possible to get either G or G' or something which is neither one. To obtain physically significant values of G, one must use a long enough specimen and avoid conditions for which torsional and flexural resonances, when considered separately, occur at the same frequency. Because of the coupling between these two types of oscillations, there results a perturbation in both the torsional and flexural frequencies, necessitating a further correction. As far as possible crystals having these troublesome lengths were not used. In actual practice many resonance responses are found and one of the major experimental difficulties lies in identifying the desired torsional one.

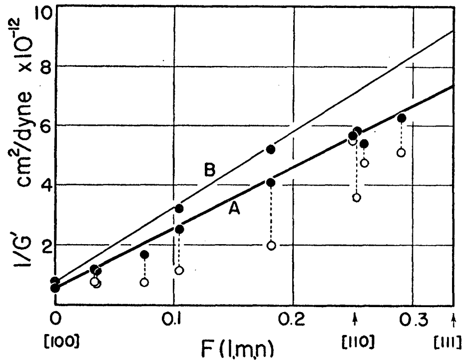

FIG. 1. Reciprocal rigidity modulus against orientation. Curve A, at room temperature. $1/G$, open circles ○. $1/G'$ closed circles ●. Dotted line, bending-torsion correction. Curve B at 466°C, just below critical temperature.

Rigidity modulus measurements were made at room temperature on ten crystals having orientation functions: 0.0017, 0.034, 0.035, 0.075, 0.107, 0.180, 0.248, 0.254, 0.258, 0.290. The modulus of three crystals was found as a function of temperature from 25° to 500°C. The electrical apparatus, the furnace and the procedure for carrying out temperature measurements were substantially the same as used by Rinehart.[4]

RESULTS

Figure 1 shows $1/G$ and $1/G'$ plotted against F (l, m, n) for the ten crystals. Curve A represents data at room temperature. The open circles are measured values of $1/G$ [$G=G^*$, Eq. (2)]. The closed circles show the values of $1/G'$ as calculated from Eq. (5). The length of the dotted connecting line between each pair of points represents the value of the bending-torsion correction. As may be easily seen this term is surprisingly large for some of the crystals. In view of this, the curve A (also B, see later) was not drawn, as it might have been, so as to give the best fit with the points (solid circles, ●), but its

---

[13] If one defines G' as the "true" rigidity modulus then the word "correction" is fitting; if not, perhaps "bending-torsion difference" would be suitable.

[14] F. Rose, Phys. Rev. **49**, 50 (1936); M. Durand, Phys. Rev. **50**, 449 (1936).

[15] S. L. Quimby and S. Siegel, Phys. Rev. **54**, 293 (1938).

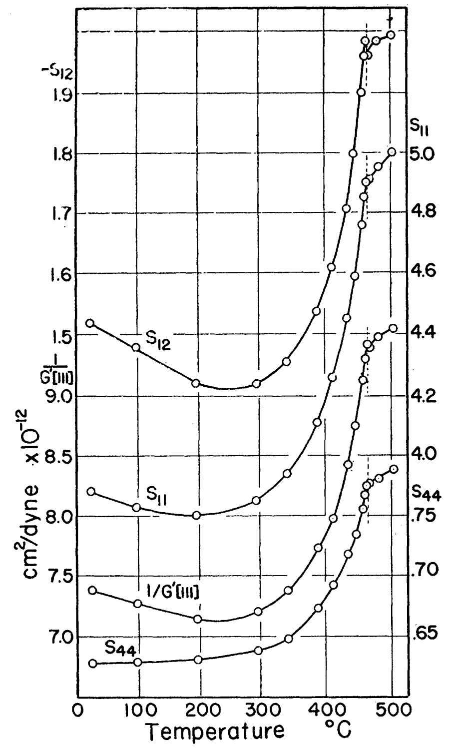

FIG. 2. The values of $1/G'$ [111] and the principal elastic parameters, s_{11}, s_{12} and s_{44} against temperature.

position is partially based on Rinehart's data as follows. He measured the Young's modulus, E, as a function of orientation, F, and plotted the relation:

$$\frac{1}{E}=s_{11}-2sF, \qquad (6)$$

which is similar in form to Eq. (3). Both (3) and (6) yield independent determinations of s, i.e., the slope of (6) is $-2s$ while the slope of (3) is $+4s$. However, since Rinehart's value of s is determined without the introduction of the bending-torsion term, it is believed to be more accurate than one that might be taken from these data. Thus curve A has been drawn through the almost zero correction crystal ($F=0.0017$) with twice the slope determined by Rinehart. The other crystal ($F=0.248$) with a small correction lies practically on the line so drawn. The remaining points, considering again how much they have been "corrected," lie surprisingly near the curve and seem to give good justification both for the experimental method used and its interpretation. It should be emphasized that the calculation of the bending-torsion correction is not proportional to, or simply dependent on, the orientation function, F, but depends in a rather complicated way on the direction cosines, l, m and n. Two crystals may have the same orientation function, F, but differ widely in the correction (see Fig. 1, $F=0.25$). Moreover the accuracy of determining the correction from the measured l, m and n is not as high as the determination of F from the same data. Curve B, Fig. 1, shows the modulus, $1/G'$, at 466°C, which is just below the critical temperature (468°C) for order-disorder. This curve was drawn in the same fashion as curve A, i.e., through the point for $F=0.0017$ and with the slope based similarly on Rinehart's data at that temperature.

The value of $1/G'$ for the crystal, $F=0.0017$, is practically s_{44} [Eq. (3), $F\doteq 0$]. Thus the reciprocal modulus of that crystal as a function of temperature is also the value of s_{44} as a function of temperature. The temperature dependence of s_{44} is shown graphically in Fig. 2. Also shown are s_{11} (Rinehart's determination); and s_{12} which is calculated from s_{11}, s_{44}, and s. The s_{44} varies little up to 300°C where the slope starts to increase rapidly, due to the rapid disordering, becoming very large as the critical temperature (468°C, indicated by dotted line) is reached. The critical temperature is well marked by the definite discontinuity in the slope. This is supposed to be the final and complete disappearance of order. Although similar in shape to s_{11}, the s_{44} does not have the unusual negative slope exhibited by s_{11} at room temperature. The s_{12} curve, however, does show this negative slope characteristic, as does $1/G'$ [111]. This contrasts markedly with the fact that Siegel's s_{11}, s_{12} and s_{44} for Cu_3Au

TABLE I. *Principal elastic parameters of beta-brass at various temperatures.*

	ELASTIC PARAMETERS (10^{-12} cm²/dyne)		
T°C	s_{11}	$-s_{12}$	s_{44}
24	3.88	1.52	0.578
195	3.61	1.42	0.580
293	3.87	1.42	0.588
389	4.15	1.53	0.624
448	4.64	1.80	0.685
466	4.96	1.98	0.725
468Tc	4.97	1.96	0.727
506	5.06	1.99	0.739

all slope positively at room temperature. The variation of these beta-brass parameters seems to be in general agreement with other order-dependent quantities such as specific heat,[16] resistivity[3] and the determination of Young's modulus[17] for polycrystalline beta-brass. Values of s_{11}, s_{12} and s_{44} are given at selected temperatures in Table I.

Knowledge of the temperature-dependence of the three elastic parameters s_{11}, s_{12} and s_{44} allows the calculation of the behavior of the elasticity in any direction at any temperature. The value of $1/G'[111]$ (reciprocal of the rigidity modulus in the $[111]$ direction) has been calculated from these data and is shown in Fig. 2. It again shows the initial negative slope before much disorder sets in.

The ratio of maximum to minimum modulus in the $[100]$ and $[111]$ directions is taken, as was done by Webb[3] and Rinehart,[4] as a measure of the elastic anisotropy. Figure 1, curve B shows greater anisotropy at the higher temperature than curve A at room temperature, although both anisotropies are large. The dependence of anisotropy on temperature is shown in Fig. 3, curve A. The anisotropy in the rigidity modulus agrees well in shape with the similar Young's modulus anisotropy, but has a larger absolute value (12.8 compared to 8.2 at room temperature).

The compressibility, k, may be found from

$$k = 3(s_{11} + 2s_{12}). \qquad (7)$$

It[18] was computed as a function of the temperature and plotted in Fig. 3 curve B. Unfortunately the quantity k, depends upon the difference between two almost equal quantities, thus making it very sensitive to slight changes in s_{11} and s_{12}. Therefore the accuracy of the compressibility curve is not great, but probably sufficient to show the general trend. The compressibility increases with temperature almost to the critical temperature where it suffers a rather rapid decrease, to rise again just beyond the critical temperature. It would be interesting to check the genuineness of this dip by a direct measurement of compressibility as a function of temperature.

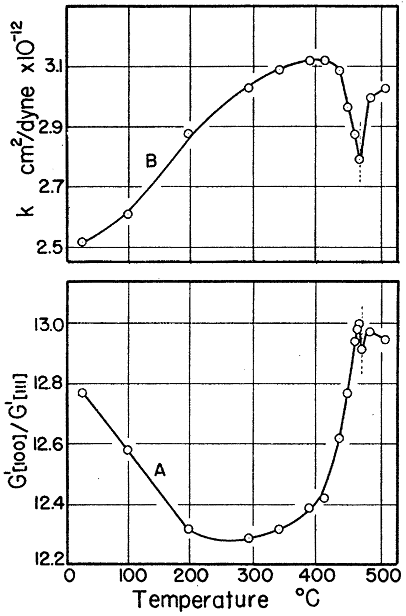

FIG. 3. Curve A, anisotropy, $G'[100]/G'[111]$, in rigidity modulus against temperature. Curve B, computed compressibility against temperature.

Perhaps this change may be correlated with the thermal volume expansion[11] which also undergoes a discontinuity at the critical temperature.

In conclusion, the writer gratefully acknowledges his indebtedness to Professor E. P. T. Tyndall for much helpful advice and many valuable suggestions; 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.

---

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

[17] W. Köster, discussion of paper by G. Borelius, Zeits. f. Elektrochemie **45**, 16 (1938).

[18] S. Lussana, Nuovo Cimento **19** (1910), gives a value 1.62×10^{-12} cm^2/dyne for this composition of brass at room temperature. However, his values of k for copper and zinc do not agree with Bridgman's; so there exists some doubt about Lussana's value for beta-brass.