

ture dependence of the exchange resonance is presumed to arise from a large magnetocrystalline anisotropy energy as in SmIG. Supplementary transmission measurements with samples of HoGaG and 5% Ho-YIG indicate that most of the remaining absorptions in the iron garnet are probably transitions to higher crystal field levels as modified by the iron exchange field.

The absence of any observable magnetic absorption spectrum in GdIG ($L=0$) validates our conclusion that the strength of single rare-earth ion transitions is determined by the anisotropy and corresponding inequival-

ence of the rare-earth ions produced by local crystalline electric fields at the various types of sites.

ACKNOWLEDGMENTS

We wish to thank Professor R. V. Jones, of Harvard, for the pressed powders of rare-earth iron garnets. We would also like to thank Dr. K. A. Wickersheim and Dr. R. L. White of the General Telephone Research Laboratory for helpful discussions and for supplying, with Dr. R. A. Lefever and his co-workers, many of the single crystals used in these experiments.

Elastic Properties of β -CuZn

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(Received 19 October 1962)

The elastic moduli of a single crystal of stoichiometric β -CuZn have been measured as a function of temperature in the range 4.2 to 800°K. The temperature variation was found to be normal for all elastic constants. In particular, c_{11} is unchanged on passing through the critical temperature T_c , while the shear constants C and C' exhibit a substantial change at T_c . This change is consistent with the configurational change due to disordering.

Measurements were also made on the composition dependence of the room-temperature elastic constants in the β field. A large variation with composition was found, amounting to almost 100% for the shear constant C' . This behavior is in qualitative agreement with theory, and suggests substantial contributions to the elastic moduli from second-neighbor interactions and the Fermi surface overlap.

I. INTRODUCTION

THE temperature and composition dependence of the elastic moduli of β -CuZn have attracted considerable experimental and theoretical interest. In previous work the shear constant C' showed an anomalous increase with increasing temperature,¹ and for off-stoichiometric alloys the ratio C/C' was found to be abnormally large.² These observations were basically involved with the question of the stability of β -phase alloys, and this was investigated by Jones³ and by Zener.⁴ Jones found the β phase in CuZn to be rendered stable by a large contribution to the shear constants from the overlap of the Fermi surface with the Brillouin zone. Such an effect is not unexpected, since a bcc lattice of hard spheres will offer no resistance to a (110) $[\bar{1}10]$ shear. Thus, the system will be unstable, so that in the real lattice the electrostatic interaction, second-neighbor terms, and the Fermi overlap must combine to offset the nearest-neighbor repulsive con-

tribution to C' . In the absence of second-neighbor interactions, a substantial electronic contribution to the shear constants is not unreasonable. With second-neighbor interactions, however, the electronic contribution becomes less clearly defined. Because these effects should depend sensitively on composition, in the present work we have studied the composition dependence of the room-temperature elastic constants in the β phase. To assist our understanding of second-neighbor effects, we have also examined the temperature dependence of the elastic constants of an alloy of equiatomic composition.

II. EXPERIMENTAL RESULTS

The single crystals used in this experiment were grown by the Bridgman method, using graphite crucibles sealed under a partial pressure of argon in vycor tubes. After suitable orientation by Laue photographs, specimens were cut from the crystals and machined to have exposed faces perpendicular to both the $[100]$ and $[110]$ directions. These faces were lapped optically flat and finished to parallelism to within 0.0001 in. The material used for the alloys was 99.99% pure copper and 99.99% pure zinc. Several alloys made from high purity copper and zinc (99.999%) gave room-temperature elastic constants in agreement with corresponding

¹ J. S. Rinehart, Phys. Rev. **58**, 365 (1940); **59**, 308 (1941); R. A. Artman, J. Appl. Phys. **23**, 475 (1952).

² W. Webb, Phys. Rev. **55**, 297 (1939); J. S. Rinehart, *ibid.* **58**, 365 (1940); **59**, 308 (1941). See also D. Lazarus, *ibid.* **76**, 545 (1949).

³ H. Jones, Phil. Mag. **43**, 105 (1952). See also, I. Isenberg, Phys. Rev. **83**, 637 (1951).

⁴ C. Zener, Phys. Rev. **71**, 846 (1947).

alloys of lower purity material. Alloys were grown with zinc contents of 45.0, 46.0, 47.8, 48.8, and 50.0 at.-%.

To determine the elastic constants, ultrasonic pulse measurements were made in the usual fashion.⁵ The low-temperature data were obtained in a manner already described,⁶ and need no further comment. For high-temperature measurements, the crystal was held by molybdenum leaf springs onto a copper base, which was heated from below by a fine wire spiral heater. The transducer was bonded to the crystal with Sauereisen P31 cement, and the contact to the transducer made by a molybdenum spring. This assembly was held in a small ceramic container, which mounted into a vacuum-tight water-cooled brass can, filled to a partial pressure with argon. When packed with insulating cloth, this device was steady to better than 1°C over times long compared to the measuring interval. The temperatures were measured with a potentiometer and a chromel-alumel thermocouple mounted in the base on which the crystal was held. To guard against a possible loss of zinc at high temperatures, the ceramic container was filled with chips from the original crystal. Repetition of measurements before and after heating yielded the same results. Data were taken from 4 to 700°K at every 20°K, and every 10°K from 700 to 800°K, the critical temperature being at approximately 735°K.⁷ Elastic constants were obtained from the wave velocities using the densities determined by Beck and Smith⁸ and the coefficient of thermal expansion due to Owen and Pickup.⁹

III. EXPERIMENTAL RESULTS

The temperature variation of the elastic constants of a single crystal of β -CuZn (50.0% Zn) is shown in Figs. 1-3. An estimate of 1% for the over-all random error in the elastic constants has been taken in drawing

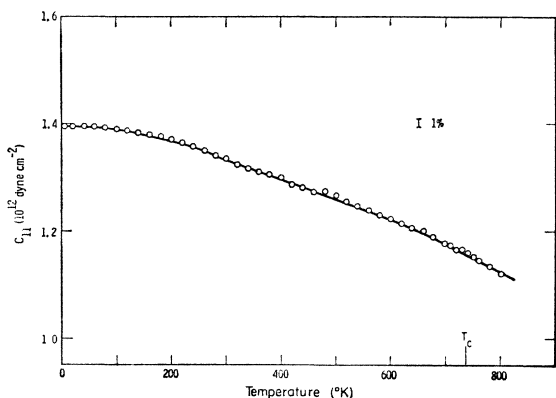


FIG. 1. The temperature variation of c_{11} .

⁵ J. A. Rayne, Phys. Rev. **112**, 1125 (1958).

⁶ J. A. Rayne, Phys. Rev. **115**, 63 (1959).

⁷ D. Chipman and B. E. Warren, J. Appl. Phys. **21**, 696 (1950).

⁸ L. H. Beck and C. S. Smith, J. Metals **4**, 1079 (1952).

⁹ E. A. Owen and L. Pickup, Proc. Roy. Soc. (London) **A145**, 258 (1934).

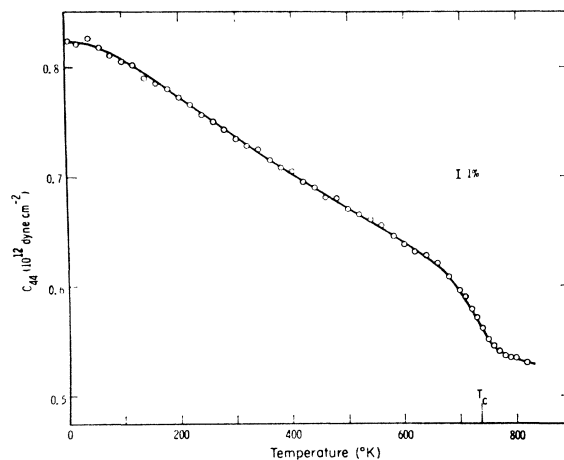


FIG. 2. The temperature variation of the shear constant $C = c_{44}$.

these curves. Systematic errors, which leave the relative variation of the elastic constants unchanged, have not been considered. All of the elastic constants behave normally with temperature, in disagreement with previous work.¹ The longitudinal mode c_{11} shows virtually no change on passing through T_c , indicating that the contribution of the electron gas to the elastic constants does not change from the ordered to the disordered state. Therefore, that part of the variation of the elastic constants due to changes in the Fermi energy with temperature must be small.

Unlike c_{11} , the shear constants C and C' show a substantial change in the vicinity of the critical temperature. Data above the critical temperature are limited because of the high ultrasonic attenuation, particularly in C' , and the α - β transformation of the quartz transducer. The low temperature data, extrapolated to 0°K, give a Debye $\theta = 288 \pm 2^\circ\text{K}$, in good agreement with the value obtained from heat capacity measurements.¹⁰

In Fig. 4 the composition dependence of the elastic moduli of β brass is shown. A drastic variation with

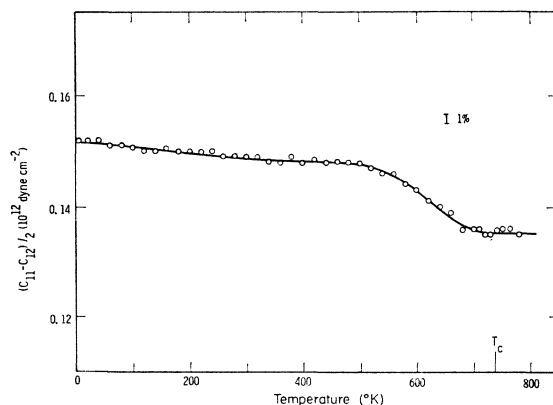


FIG. 3. The temperature variation of the shear constant $C' = \frac{1}{2}(c_{11} - c_{12})$.

¹⁰ B. W. Veal and J. A. Rayne, Phys. Rev. **128**, 551 (1962).

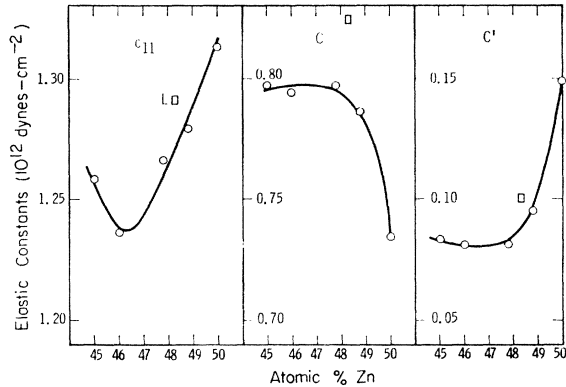


Fig. 4. Composition dependence of the elastic moduli in the β field. The squares represent the data of Lazarus (reference 2).

composition is clearly evident, this variation being almost 100% for C' . A reversal in the elastic constants is well defined in c_{11} , but not clearly resolved in C' and C . The squares in Fig. 4 represent the data of Lazarus,² which differ from the present determinations by about 3% for c_{11} and C , and by 10% for C' . We can present no satisfactory explanation for these discrepancies.

IV. DISCUSSION

If we neglect for the moment the Fermi energy, the contributions to the elastic constants from the ion-core exchange interactions and the electrostatic interaction can be calculated explicitly for β brass of equiatomic composition. For the Coulomb part of the elastic constants, we assume β brass to be derived from the superposition of a CsCl lattice of charges $\pm\frac{1}{2}$, and bcc lattice of charge $\frac{2}{3}$. The bcc contributions have been given by Fuchs,¹¹ and the CsCl contribution calculated by the method of Born and Misra.¹² This gives for ordered β brass, in units of 10^{12} dyn/cm²:

$$c_{11}=0.775, \quad C=0.499, \quad C'=0.138,$$

and for the disordered state:

$$c_{11}=0.637, \quad C=0.502, \quad C'=0.068.$$

To calculate the ion-core interaction, we assume that the potential W has the same form for all atom pairs of the alloy, i.e., $W_{AB}=\phi_{AB}e^{-x}$, $W_{AA}=\phi_{AA}e^{-x}$, etc. This is done for both first- and second-neighbor interactions: for nearest neighbors $x_1=r/\rho_1$, and for nearest neighbors $x_2=l/\rho_2$. Here, $r=\sqrt{3}a_0/2$, $l=a_0$; ρ_1 and ρ_2 are constants and a_0 is the lattice parameter. For first neighbors the exchange contributions are

$$C' = -\frac{4}{3}x_1W_1, \quad C = (4/9)x_1(x_1-2)W_1, \quad (1)$$

and for second neighbors

$$C' = \frac{1}{2}x_2(x_2-1)W_2, \quad C = -x_2W_2. \quad (2)$$

It is not profitable to use this analysis for c_{11} , since c_{11} contains a term depending on the energy change of the lowest state of the conduction electrons with volume; this term is absent from C and C' . We remark only that the first-neighbor ionic contribution to c_{11} is the same as that for C .

The inadequacy of the nearest-neighbor approximation can be shown in two ways: The Fermi contributions to the shear constants given by Jones,³ when used with the 0°K elastic constants, yields the impossible result $x_1 \sim -300$. To obtain a reasonable value, e.g., $x_1 \sim 10$, the Fermi contributions would have to be increased by almost an order of magnitude. Another determination can be made by taking the difference of each shear constant in the ordered and disordered state, thereby eliminating the Fermi terms, and then solving the two equations for x_1 . Taking 800°K as the "disordered" state gives $x_1=25$, while any extrapolation to complete disorder only increases this value.

It is, therefore, necessary to invoke a substantial second-neighbor contribution to the shear moduli, or a large noncentral interaction, in order to give even a qualitative discussion of the observed temperature variation. Assuming a second-neighbor term, the ionic contributions to the shear constants can be written in terms of the Cowley¹³ short-range order parameters α_1 and α_2 : at perfect order $\alpha_1=-1$ and $\alpha_2=1$; at perfect disorder $\alpha_1=\alpha_2=0$. A straightforward calculation gives for (1) and (2):

$$\begin{aligned} C' &= -\frac{1}{3}x_1(U_1+\alpha_1V_1) + \frac{1}{8}x_2(x_2-1)(U_2+\alpha_2V_2), \\ C &= \frac{1}{3}x_1(x_1-2)(U_1+\alpha_1V_1) - \frac{1}{4}x_2(U_2+\alpha_2V_2), \end{aligned} \quad (3)$$

where U and V have the same form for both first and second neighbors:

$$\begin{aligned} U &= \phi_{AA} + \phi_{BB} + 2\phi_{AB}, \\ V &= \phi_{AA} + \phi_{BB} - 2\phi_{AB}. \end{aligned}$$

With only first-neighbor interactions, C' would increase with temperature, since $(U_1+\alpha_1V_1)$ decreases with T . It is the second-neighbor term that causes C' to behave normally with temperature. These two terms almost balance in C' , while in C the first-neighbor term is dominant. The qualitative behavior of the elastic constants with T then follows: The discontinuities in C and C' arise from the rapid variation of α_1 and α_2 in the vicinity of T_c .¹⁴ These variations are additive in the shear constants (since $\alpha_1 < 0$), but presumably of opposite sign in c_{11} , so that no configurational discontinuity is seen in the bulk modulus. Since the electrostatic contribution to C is almost constant with temperature, the linear variation of C with T should be contained in the ionic terms. Calling the electrostatic part C_{e1} and $\Delta C = C - C_{e1}$, a simple manipulation gives

$$(d/dt)(\ln \Delta C) \cong \bar{x}\beta,$$

¹¹ K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1936).

¹² R. D. Misra, Proc. Cambridge Phil Soc. **36**, 173 (1940).

¹³ J. M. Cowley, Phys. Rev. **77**, 669 (1950).

¹⁴ P. A. Flinn and G. M. McManus, Phys. Rev. **124**, 54 (1961).

where β is the linear expansion coefficient, approximately $2.6 \times 10^{-5}/^\circ\text{K}$. In this we have ignored terms in $d\alpha/dT$, since these are negligible except near T_c . The unknown \bar{x} is

$$\bar{x} \cong x_1 - 2 - \text{terms of order } (x_2 - x_1)/x_1x_2.$$

In this first approximation, using only $x_1 - 2 = \bar{x}$, the slope of $\ln\Delta C$ gives $x_1 \cong 15$, and, therefore, since $r = 2.56 \text{ \AA}$, $\rho \sim 0.17 \text{ \AA}$. This is also the slope of c_{11} with T , which is not unexpected if the electronic and electrostatic terms in the bulk modulus do not change much except near T_c .

The large number of unknowns in Eq. (3) makes it impossible to determine all of the variables from the available data. It is clear, however, that a second-neighbor approximation is sufficient to explain the features of the temperature variation of the elastic constituents. The contributions from the Fermi surface overlap, while appreciable, are insufficient to explain the observed behavior in the nearest-neighbor approximation.

To describe the composition dependence of the elastic moduli, some of the same considerations apply as those used in the above discussion. In Eqs. (1) and (2), the term W_1 decreases with increasing zinc concentration, while W_2 increases with increasing zinc content. The Fermi contribution increases for both C and C' , and for c_{11} the volume-dependent electronic term¹⁵ increases also, as the zinc content is increased. The bulk modulus will, therefore, show a decrease due to W_1 and then an increase due to W_2 and the electronic term as the equiatomic composition is approached. For the shear constant C , the second-neighbor term becomes more negative, so the entire ionic contribution decreases, and C decreases despite the increasing Fermi term. Similarly, in C' all of the terms are increasing, and hence C' shows a drastic increase as the limit of the β region is approached. For all of the elastic constants, the variation

of the electrostatic contribution is of minor importance.¹⁵ In view of these considerations, the anomalous increase of C' with temperature¹ is readily explained: Since W_2 decreases and W_1 increases as the copper content is increased, when W_2 is small enough the first-neighbor term will be dominant and hence C' will increase with increasing temperature. This should occur where C' is a minimum; that is, for alloys with zinc concentration $\lesssim 47\%$, as observed.¹ As before, however, the presence of the second-neighbor interactions makes it impossible to estimate the amounts of the ionic contributions or the Fermi surface overlap. Since both W_2 and the overlap term are increasing with increasing zinc, it is not possible to separate these two effects. It is apparent that it is not just the overlap contribution, but also the second-neighbor exchange terms that lead to the stability of the β -phase CuZn alloys.

V. CONCLUSIONS

The temperature dependence of the elastic moduli of CuZn indicates that second-neighbor ion exchange interactions make a substantial contribution to the shear constants. The ionic terms show the proper behavior with composition to explain the variation of the elastic moduli in the β -phase region, but it is not possible to separate the contributions from the second-neighbor interaction and the Fermi surface overlap, since both have the same composition dependence. The anomaly in the temperature variation of the elastic constants of off-stoichiometric alloys is explainable by this model.

ACKNOWLEDGMENTS

The author would like to thank P. C. Hodder for growing the crystals used in this study; R. Farich for the preparation of the ultrasonic specimens; and B. W. Veal, P. A. Flinn, and A. A. Maradudin for much helpful advice and counsel. The valuable assistance of J. A. Rayne is gratefully acknowledged.

¹⁵ H. Jones, J. Appl. Phys. **23**, 697 (1952).