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Elastic Constants of α-Brasses: Variation with Solute Concentration from 4.2–300°K

J. A. Rayne
Westinghouse Electric Corporation, Pittsburgh, Pennsylvania

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Elastic constant measurements have been made on a representative series of α-brasses in the temperature range 4.2–300°K. No appreciable change with temperature occurs in the dependence of C and C' on solute concentration. Possible explanations for this result are considered. The Θ values for the alloys, as computed for the elastic-constant data at 4.2°K, differ significantly from the calorimetric values. It is believed that this discrepancy results from the difference between the phonon wavelengths used in the ultrasonic measurements and those contributing to the lattice heat capacity of the alloys at low temperatures.

INTRODUCTION

FOLLOWING recent work[1] on the variation with solute concentration of the room temperature elastic constants of the α-brasses, it was considered of interest to extend the measurements to liquid helium temperatures. Thus the overlap contribution to c_{44}, resulting from the intersection of the Fermi surface with the $\{111\}$ faces of the Brillouin zone, might be expected to become more prominent at low temperatures owing to the less diffuse nature of the electron distribution function. Such a situation should cause an appreciable change in the concentration dependence of c_{44} and also should give rise to an anomalous variation with zinc content of the apparent electronic heat capacity of the alloys. The latter effect has already been discussed by Jones.[2] In addition, liquid helium measurements would enable a comparison to be made between the Debye temperatures for the alloys obtained from calorimetric data[3] and from the theory[4] of the phonon spectrum of solids at low temperatures. This comparison is of some importance, since it is necessary to know to what extent elastic-constant data can be used to predict the lattice heat capacity of alloys at low temperatures.

EXPERIMENTAL

A description of the methods of measurement and specimen preparation has been given in a previous paper[1] and requires no further elaboration. Details of the cryostat are shown in Fig. 1. The coaxial feed A, which also acts as a supporting member of the assembly, brings 10 Mc/sec pulses to the transducer B through the spring-loaded plunger C. The latter consists of an inner copper electrode surrounded by a recessed insulating disk, which serves to center the transducer. To enable the latter to be oriented in a fixed position relative to the specimen, the plunger is prevented from rotation by means of a peg D sliding in the slotted insulator E. In this way, a Y-cut transducer may be bonded to the crystal at low temperatures so as to produce a shear wave of the desired polarization.

The specimen F is mounted in a spring-loaded plastic cup G oriented in the copper sleeve H. This sleeve is keyed onto the spacer J and can be moved vertically by means of the stainless steel tube K, which slides in an O-ring seal at the top of the cryostat. When the specimen is lowered onto the stage L, it makes contact with the upper plated face of the transducer and hence completes the electrical path for the rf pulse. A platinum resistance thermometer M mounted on the stage L serves to indicate its temperature. Values of the latter between 300°K and 77°K are obtained by

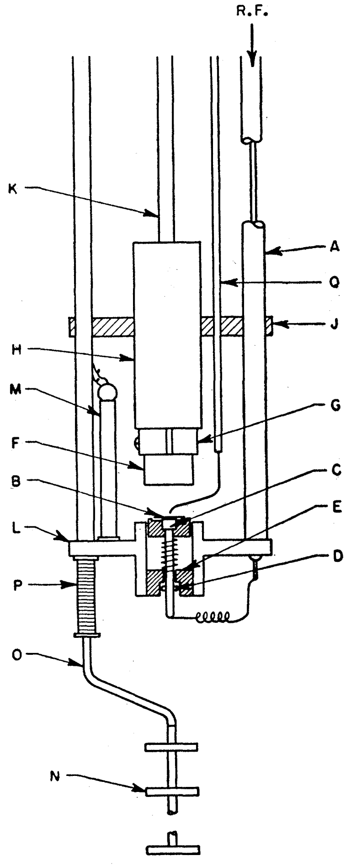

FIG. 1. Details of cryostat for low-temperature elastic constant measurements.

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[1] J. A. Rayne, Phys. Rev. **112**, 1125 (1958).
[2] H. Jones, Proc. Roy. Soc. (London) **A240**, 321 (1957).
[3] J. A. Rayne, Phys. Rev. **108**, 22 (1957).
[4] J. de Launay, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 285.

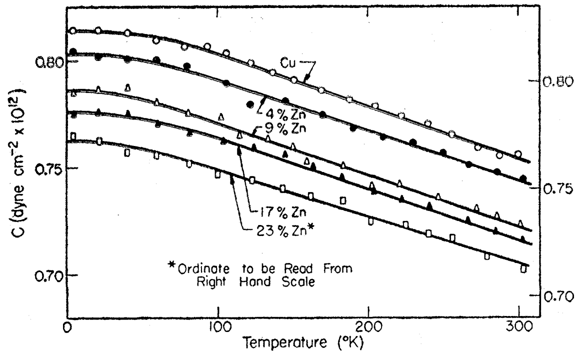

FIG. 2. Variation with temperature of shear constant C for α-brasses.

evacuating the insulating space of the helium Dewar as well as its interior, and allowing the assembly to cool down slowly with liquid nitrogen in the outer Dewar. To obtain temperatures intermediate between 4°K and 77°K, the copper vane assembly N is allowed to dip into liquid helium and the required temperature difference set up across the stainless steel tube O by means of power supplied to the heater P.

For covering the complete temperature range 4–300°K, it is necessary to use two bonding agents. Down to 120°K, glycerin applied to the transducer at room temperature gives satisfactory echos, but at lower temperatures it tends to crack. Below 120°K EPA,[5] a mixture of ether, ethyl alcohol, and isopentane is used. A drop of this solution is applied to the transducer at 120°K through the capillary Q and the specimen is then pressed onto the stage. At about 100°K the solution forms a glassy film, which gives a good acoustic bond to the specimen down to liquid helium temperatures.

In computing the elastic constants, the crystal densities at 300°K were obtained from the x-ray lattice spacings appropriate to the crystal compositions employed. For the samples of higher zinc composition, these values are significantly higher ($\sim\frac{1}{2}\%$) than the densities determined by direct macroscopic measurement, as a result of diffusion voids within the samples. It is felt, however, that if measurements of transit times are taken from the *leading* edge of the pulse, then the x-ray densities are the correct ones to use. In any event, either assumption makes little difference to the conclusions of the paper.

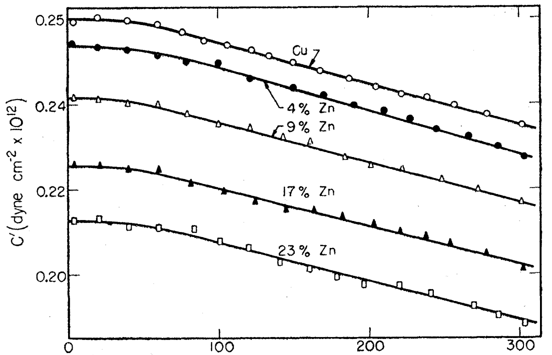

FIG. 3. Variation with temperature of shear constant C' for α-brasses.

Since there are no low-temperature thermal expansion data for the α-brasses, it is necessary to make an additional assumption in order to obtain the temperature variation of the elastic constants for the alloys. Fortunately, the correction for thermal expansion is small and there is no sensible error in assuming that in all samples it is the same as that for pure copper. In the present work, we have computed the latter using the interferometric expansion measurements of Rubin *et al.*[6]

RESULTS

Graphs giving the temperature variation of the relevant elastic constants for the various samples are shown in Figs. 2, 3, and 4. The values at 4.2°K are summarized in Table I, which also gives the estimated probable errors in the data arising from uncertainties in the velocity determinations. No definite figure can be adduced for the error arising from the presence of crystal imperfections. It is believed, however, that a figure of one percent is not an unreasonable value for the over-all random probable error in the elastic constants. This estimate has been adopted in Figs. 5 and 6, which, respectively, shown the shear constants C and C' as a function of solute concentration both at 4°K and 300°K. Systematic errors, such as transit-time effects, will not affect the *relative* variation of the elastic constants and have not been considered in drawing these curves. No limits of certainty have been placed on the points for pure copper, since the errors are substantially smaller than for the alloys because of the larger specimen length employed and the greater degree of crystal perfection.

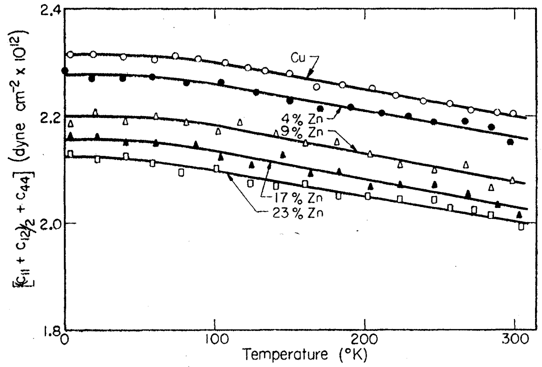

FIG. 4. Variation with temperature of $\frac{1}{2}[c_{11}+c_{12}+2c_{44}]$ for α-brasses.

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[5] W. C. Overton, Jr., and J. Gaffney, Phys. Rev. **98**, 969 (1955).

[6] Rubin, Altman, and Johnston, J. Am. Chem. Soc. **76**, 5289 (1954).

DISCUSSION

Reference to Table I shows that there is very good agreement between our values for the elastic constants of copper at 4.2°K and those of Overton and Gaffney.[5] In fact the maximum discrepancy between the two sets of measurements over the whole temperature range covered is only about one percent. Above 80°K, the present data for copper can be well represented by a linear variation with temperature, whereas that of Overton and Gaffney appears to have a slight curvature. This difference, however, is well within the limits of error and does not appear to be significant. It is believed, therefore, that the general agreement between the two sets of results constitutes adequate proof of the accuracy of our techniques and substantiates our claims for the general confidence limits of C and C'.

(a) Overlap Effects

From Figs. 2, 3, and 4 it can be seen that the curves of the temperature variation of the elastic constants for the various alloys are geometrically similar to those of copper. This is further demonstrated in Figs. 5 and 6 which show that there is no significant change in the dependence of C and C' on solute concentration between 4°K and 300°K. Such behavior is somewhat surprising in view of our previous conclusions regarding the effect of overlap on the dependence of c_{44} with solute concentration. It would be expected that, owing to the diffuseness of the Fermi distribution function at room temperature, the effects of overlap at 300°K would be less pronounced than at liquid helium temperatures. The absence of such an effect could be due to a number of causes:

TABLE I. Elastic constants of α-brasses at 4.2°K.[a]

Composition (atomic %)	c_{44} (10^{12} dyne cm^{-2})	$\frac{1}{2}(c_{11}-c_{12})$ (10^{12} dyne cm^{-2})	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$ (10^{12} dyne cm^{-2})
0	0.814±0.001 (0.818)	0.260±0.001 (0.256)	2.316±0.003 (2.323)
4.1	0.803±0.004	0.254±0.001	2.278±0.010
9.3	0.786±0.004	0.242±0.001	2.200±0.010
17.4	0.775±0.004	0.226±0.001	2.156±0.010
22.7	0.773±0.004	0.213±0.001	2.124±0.010

[a] The values in parentheses are those of Overton and Gaffney (reference 5).

(1) Microscopic inhomogeneities in the alloy specimens smear out the onset of overlap.

(2) Experimental errors are too large to show any discontinuities in the curves.

(3) Overlap is not initiated in the composition range studied.

(4) Overlap effects are modified even at absolute zero by correlation or are not present at all.

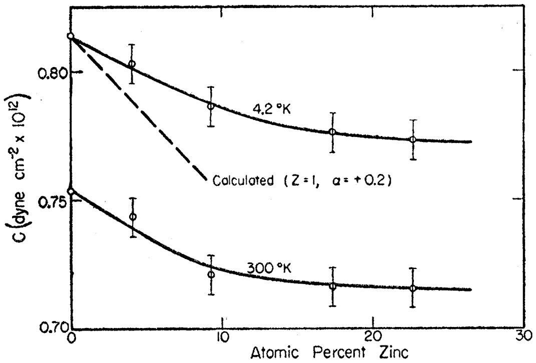

FIG. 5. Variation with solute concentration of shear constant C for α-brasses at 4.2° K and 300° K.

Of these possibilities, it is believed that a combination of the first two is the most likely explanation of the lack of any temperature effect. Local inhomogeneities are believed to play a significant role, since their presence could easily explain why the corresponding heat capacity data does not show the anomalous behavior predicted by Jones.[2]

It is, of course, impossible to eliminate the other alternatives in view of the rather precarious state of alloy theory in general. If we adopt the ideas of Cohen and Heine,[7] overlap across the {111} faces of the Brillouin zone already occurs in copper. Alloying merely alters the area of contact consistent with the general requirement that the Fermi surface becomes more spherical with increasing solute concentration. Provided that the Fermi surface does not actually break away from the zone faces, this model could easily explain the absence of a break in the concentration dependence of c_{44} at low temperatures. There is, however, a difficulty with such a viewpoint arising from the fact that the initial *decrease* in overlap would cause a negative contribution to the change in c_{44} with solute concentration. Thus, the experimental curve would lie *below* the dotted line, which represents the theoretical change in c_{44} arising from effects other than overlap.[1] Such is clearly not the case; hence it is unlikely that the present results can be explained in this way. In fact,

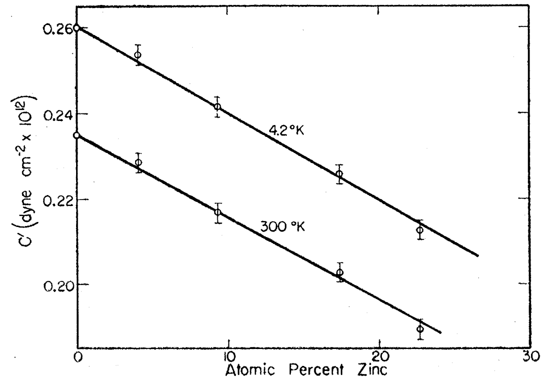

FIG. 6. Variation with solute concentration of shear constant C' for α-brasses at 4.2° K and 300° K.

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[7] M. Cohen and V. Heine, *Advances in Physics* (Taylor and Francis, Ltd., London, 1954), Vol. 7, p. 395.

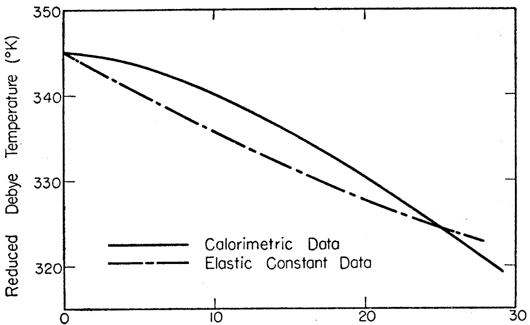

FIG. 7. Comparison of θ_r for α-brasses obtained from calorimetric and elastic constant data.

the observed behavior of the elastic constants is in definite disagreement with the Cohen and Heine model whether the Fermi surface breaks away from the zone boundary or not, so that there is considerable doubt as to whether their theory does provide a satisfactory explanation of the properties of the α-brasses.

(b) Variation of Debye Temperature with Solute Concentration

There is considerable interest in a comparison of the Debye temperatures of solids obtained from calorimetric and elastic constant data at liquid helium temperatures. In this region the simple continuum model should adequately describe the phonon spectrum of a solid, so that one would expect exact agreement between the two sets of data. Indeed, a comparison[8] of the available measurements shows that, for simple cubic metals and the alkali halides, such agreement does exist. It is of some importance (e.g., in computing the lattice contribution to the heat capacity of a system such as Cu-Mn which has a low-temperature anomaly) to know whether such agreement exists for simple alloys.

Since only long-wavelength phonons are involved at low temperatures, an alloy should presumably behave as a homogeneous solid having the same density and elastic constants. Now, according to the work of de Launay,[4] we have for a cubic solid

$$\Theta^3=\frac{9N}{8\pi V}\left(\frac{h}{k}\right)^3\left(\frac{c_{44}}{\rho}\right)^{\frac{3}{2}}\frac{9}{18+\sqrt{3}}f(s,t), \tag{1}$$

where $f(s,t)$ is a tabulated function of the variables $s=(c_{11}-c_{44})/(c_{12}+c_{44})$ and $t=(c_{12}-c_{44})/c_{44}$. As demonstrated in a previous paper,[9] Eq. (1) may be written in the form

$$\Theta_r{}^3=\alpha c_{44}{}^{\frac{3}{2}}f(s,t), \tag{2}$$

where α is a constant and the reduced Debye temperature Θ_r is given by

$$\Theta_r=\left(\frac{M}{M_0}\frac{a_0}{a}\right)^{\frac{1}{2}}, \tag{3}$$

M and a being the appropriate molar mass and lattice parameter. Hence, if the subscript zero refers to pure copper, we can readily determine the variation of Θ_r from the formula

$$\Theta_r=(\Theta_r)_0(C/C_0)^{\frac{1}{2}}(f/f_0)^{\frac{1}{3}}. \tag{4}$$

Figure 7 shows the resulting variation of Θ_r computed from Eq. (4) and that obtained from the calorimetric data.[9] Clearly there is a systematic discrepancy between the two curves, which is outside the experimental error. It is believed that this disagreement results from the difference between the phonon wavelengths employed in the ultrasonic measurements and those contributing to the low-temperature heat capacity. The principal contribution to the latter comes from those phonon wavelengths λ, given approximately by

$$\lambda\sim(\Theta/T)a, \tag{5}$$

which for $\Theta=350°\text{K}$, $T=4°\text{K}$, $a=4$ A gives $\lambda\sim350$ A. Typical values for the ultrasonic wavelengths are $\lambda\sim\frac{1}{10}$ mm. Thus, the latter would be expected to average out the microscopic inhomogeneity in the crystal structure much more effectively, and hence it is not surprising that there is a small difference in the elastic behavior for the two cases. It is to be emphasized that this difference would *not* occur in crystals of a single component or in ordered structures, thus accounting for the success of the continuum model in these cases. We conclude, therefore, that elastic-constant measurements cannot give very accurate values of the Debye temperatures even of simple cubic alloys. Thus, their use in estimating the lattice contribution to the heat capacity of an alloy exhibiting a low-temperature anomaly is somewhat limited.

CONCLUSION

From elastic constant measurements on the α-brasses in the temperature ranges 4.2–300°K, it is found that the effects of overlap on the concentration dependence of c_{44} do not become more prominent at low temperatures. It is tentatively concluded that this results from a smearing caused by microscopic inhomogeneities in composition within the samples. The differences between the values of Debye temperature obtained from the present work and those found from calorimetric data are attributed to the different phonon wavelengths employed in the ultrasonic measurements.

ACKNOWLEDGMENT

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[8] G. A. Alers and J. R. Neighbours (to be published).

[9] J. A. Rayne, Phys. Rev. **110**, 606 (1958).