

Contributions to the Theory of Beta-Phase Alloys*

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All alloys of the type of β -brass decrease their concentration range in the disordered state as the temperature is lowered. The original theory of Jones is shown to be inadequate, and the observed variation with temperature of the phase boundaries is shown to follow directly from the assumption that the β -phase has a slightly lower characteristic temperature than the neighboring phases.

Beta-brass has an extremely high elastic anisotropy. This property is in part a result of an anomalously low value of $(C_{11} - C_{12})/2$, which is shown to be interpretable in terms of lattice type and inter-ionic interactions. This interpretation also explains the positive value of the temperature coefficient of E_{100} .

1. INTRODUCTION

BETA-PHASE alloys, of which beta-brass is the prototype, are best known to physicists because they exemplify the 3/2 electron-atom rule of Hume-Rothery, and also because they furnish examples of order-disorder phenomena. The purpose of the present paper is to discuss, in a qualitative manner, the origin of certain other characteristics common to these alloys. One characteristic common to all disordered beta-phase alloys is the peculiar shape of their constitution diagram. The concentration range of a disordered beta-phase rapidly narrows as the temperature is lowered, which narrowing causes the phase to disappear unless the critical temperature for ordering is reached in time. Another property which is believed to be common to all beta-phases, but which has as yet been observed only in beta-brass, is the high elastic anisotropy, the ratio of the two shear coefficients C_{44} and $(C_{11} - C_{12})/2$ being 18. Another property which is believed common to all beta-phase alloys, but which has as yet been observed only in beta-brass, is the anomalous temperature coefficient of the elastic constants $E_{[110]}$ and $E_{[100]}$. Below 200°C the temperature coefficients of these constants are positive.

2. CONSTITUTION DIAGRAM

The constitution diagram of a typical beta-phase alloy is reproduced as Fig. 1. The narrowing of the range of the disordered phase could be

regarded merely as evidence of certain thermodynamic characteristics of this phase. Thus if this disordered phase has a higher energy per mole at 0°K than the two bordering phases, but a lower effective characteristic temperature, then it must have the general shape given in Fig. 1. The proof of this statement is elementary, but a demonstration is not superfluous, since another theory has been accepted in the current literature.^{1,2} In

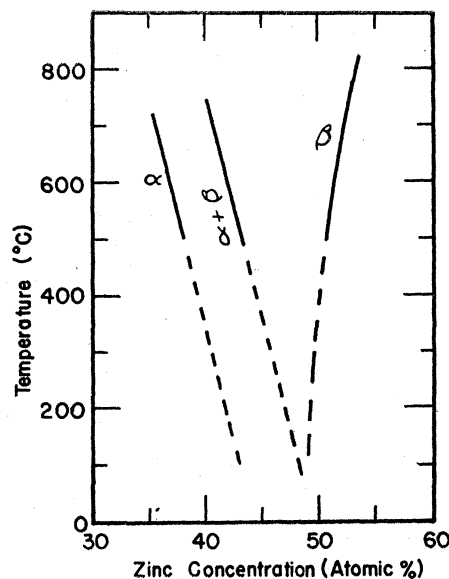


FIG. 1. Boundaries of disordered beta-phase in Cu-Zn system. Solid lines: observed. Dashed lines: extrapolation below critical temperature for ordering.

¹ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 499-502.

² W. Hume-Rothery, *The Structure of Metals and Alloys* (Institute of Metals, London, 1945) p. 83.

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this theory, developed by Jones,³ the shape of the $\alpha|(\alpha+\beta)$ and of the $(\alpha+\beta)|\beta$ boundaries presumably follows from a consideration only of the entropy of mixing and of the variation with concentration of the difference in energies of the two phases at 0°K. In view of the present confusion it appears wise to re-examine in detail the theory of these two boundaries.

An understanding of the manner in which various physical factors influence phase boundaries may best be attained through a study of the customary plot of free energy *vs.* concentration. The ordinate of this plot may be regarded as either the Helmholtz free energy F , or the Gibbs free energy G . These are essentially identical for metallic systems at atmospheric pressure. The abscissa of this plot may be either the atomic concentration X or any linear combination thereof. In order to coordinate this discussion with that of Jones, we follow his lead in expressing free energy in units of electron volts per atom, and concentration in terms of number of valence electrons per atom n . In our present case of a divalent metal dissolved in a monovalent metal, n and X are related by $n = X + 1$. A standard F *vs.* n plot does not differentiate sufficiently between the α - and β -phases to be useful for a graphical solution. Sufficient dispersion is obtained, however, by introducing a simple shear parallel to the vertical axis, i.e., by plotting $(F - fn)$ *vs.* n . The coefficient f is to be so chosen that both $(F_\alpha - fn)$ and $(F_\beta - fn)$ have minima in the desired range. Such a homogeneous shear leaves unchanged the essential property of a free energy *vs.* concentration plot, namely that the boundaries of the two phases are given by the points of contact of a common tangent.

A sheared free energy plot is presented in Fig. 2 for 0°K from the theoretical computations given by Jones, in which computations it was implicitly assumed that the β -phase remains disordered throughout the entire temperature range. From this figure it may be seen that the points of contact of a common tangent, and hence the $\alpha|(\alpha+\beta)$ and the $(\alpha+\beta)|\beta$ boundaries, are at n values of 1.41 and 1.45, respectively, values previously obtained by Jones.

In order to find the temperature variation of

³ H. Jones, Proc. Phys. Soc. London 49, pp. 243 and 250 (1937).

the phase boundaries, Jones⁴ separates the free energy of each phase in the customary manner

$$F_j(X_j, T) = f_j(X_j, T) - TS_m^{(j)}(X_j), \quad j = \alpha, \beta. \quad (1)$$

Here X_j is the atomic concentration in phase j , $S_m^{(j)}$ is the mixing entropy

$$S_m^{(j)}(X_j) = -k\{X_j \ln X_j + (1 - X_j) \ln(1 - X_j)\}, \quad (2)$$

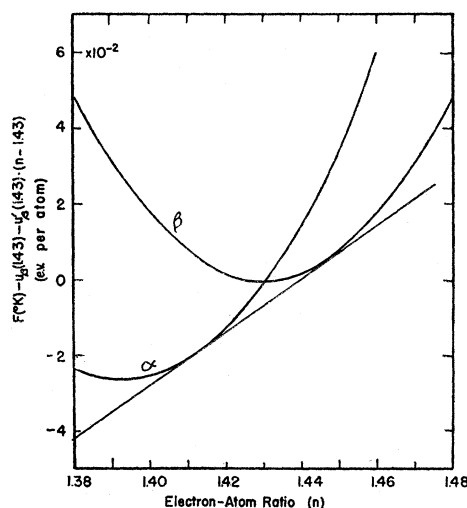


FIG. 2. Sheared free energy-concentration plot for Cu-Zn system.

and

$$f_j(X_j, T) = U_j(X_j) + \int_0^T C_j dT - T \int_0^T T^{-1} C_j dT, \quad (3)$$

U_j being the energy at 0°K. Later in his analysis Jones introduces⁵ the simplification

$$f_\alpha(X_\alpha, T) - f_\beta(X_\beta, T) = U_\alpha(X_\alpha) - U_\beta(X_\beta). \quad (4)$$

In the purely analytical method adopted by Jones, where one deals exclusively with the concentrations X_α and X_β at the two boundaries, the seriousness of this approximation is not obvious. In the graphical approach of the present discussion, we have only the one variable X (or n).

⁴ H. Jones, reference 3, p. 244.

⁵ H. Jones, reference 3, p. 256.

Thus Eqs. (1) and (2) become

$$F_j(X, T) = f_j(X, T) + kT\{X \ln X + (1-X) \ln(1-X)\}, \quad (5)$$

and Eq. (4) becomes

$$f_\alpha(X, T) - f_\beta(X, T) = U_\alpha(X) - U_\beta(X). \quad (6)$$

Upon combining these two equations one obtains

$$F_\alpha(X, T) - F_\beta(X, T) = U_\alpha(X) - U_\beta(X).$$

The approximation (4) is therefore equivalent to the assumption that temperature changes alter $F_\alpha(X)$ and $F_\beta(X)$ in precisely the same manner, a change which might be visualized as a non-homogeneous shear

$$F - fn \rightarrow F - fn - TS_m(n)$$

of Fig. 2. Such a shear will always leave the two points of tangency on opposite sides of $n=1.43$, at which value U_α and U_β are equal. Since $-TS(n)$ is convex towards the n axis, the two points of tangency will both move closer to $n=1.43$ with increasing temperature. The assumption (4) therefore leads to computed phase boundaries as shown in Fig. 3 by solid curves. The dashed curves, given by Jones, could therefore have been obtained from assumption (4) only through a mathematical error in computation.

In order to obtain the type of variation of phase boundaries actually observed, appropriate account must be taken of the differences in the thermodynamic properties of the two phases. At temperatures above the characteristic temperature of each phase the free energy per atom may be written

$$F_j(X, T) = U_j(X) + kT\{X \ln X + (1-X) \ln(1-X)\} - 3kT \ln(kT/h\nu_j), \quad (7)$$

where ν_j denotes the geometrical mean of the frequencies of all the normal modes of vibration. Equation (6) must therefore be replaced by

$$f_\alpha(X, T) - f_\beta(X, T) = U_\alpha(X) - U_\beta(X) + 3kT \ln(\nu_\alpha/\nu_\beta). \quad (8)$$

The difference in thermodynamic properties of the two phases is thus determined by the ratio ν_α/ν_β .

The equations for the phase boundaries X_α, X_β

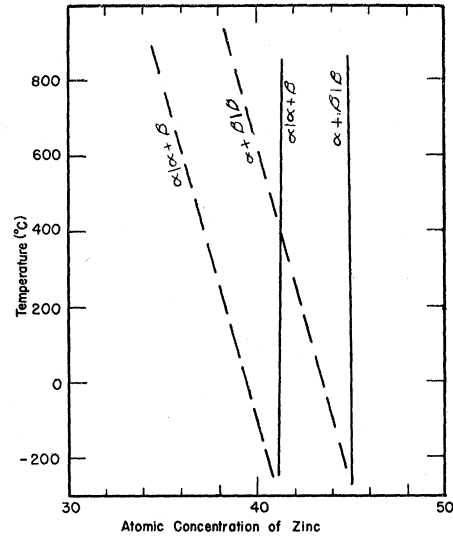


FIG. 3. $\alpha|\alpha+\beta$ and $(\alpha+\beta)|\beta$ boundaries in Cu-Zn system according to theory of Jones, as computed by author (—), as computed by Jones (---).

may be written as

$$F_\alpha'(X_\alpha) = F_\beta'(X_\beta) \quad (9)$$

$$F_\beta(X_\beta) - F_\alpha(X_\alpha) = (X_\beta - X_\alpha) \cdot \{F_\alpha'(X_\alpha) + F_\beta'(X_\beta)\}/2. \quad (10)$$

In order to facilitate the solution of these equations we utilize the experimental observations that the boundaries are confined to a comparatively narrow range of X . We therefore expand F_α and F_β as a power series in $(X - X_0)$, where X_0 is some concentration that lies within the range of interest. In order to reduce the number of physical constants, we shall assume that $U_\alpha''(X) = U_\beta''(X)$, and that ν_α and ν_β are independent of X , which assumptions lead to $F_\alpha''(X) = F_\beta''(X)$. Our expansion therefore becomes

$$\begin{aligned} F_\alpha(X, T) &= A_\alpha + B_\alpha(X - X_0) + \frac{1}{2}C(X - X_0)^2 \\ F_\beta(X, T) &= A_\beta + B_\beta(X - X_0) + \frac{1}{2}C(X - X_0)^2. \end{aligned} \quad (11)$$

Substitution of these expansions into the equilibrium Eqs. (9) and (10) leads to the solutions

$$X_\beta - X_\alpha = (B_\alpha - B_\beta)/C \quad (12)$$

$$(X_\beta + X_\alpha)/2 = X_0 - (A_\alpha - A_\beta)/(B_\alpha - B_\beta), \quad (13)$$

where

$$A_\alpha - A_\beta = U_\alpha(X_0) - U_\beta(X_0) + 3kT \ln(\nu_\alpha/\nu_\beta) \quad (14)$$

$$B_\alpha - B_\beta = U_\alpha'(X_0) - U_\beta'(X_0) \quad (15)$$

$$C = U_\alpha''(X_0) + kT/X_0(1 - X_0). \quad (16)$$

The solutions given by Eqs. (12) and (13) contain four adjustable constants, namely $U_\alpha(X_0) - U_\beta(X_0)$, $U'_\alpha(X_0) - U'_\beta(X_0)$, $U''(X_0)$, and ν_α/ν_β . On the other hand, since the two boundaries may be represented by two essentially straight lines, the experimental boundaries may likewise be represented by four constants. Agreement with experiment can therefore be forced by appropriate choice of constants. Now Jones has computed the first three constants from considerations based solely upon differences in type of the Brillouin zones of the two phases. It is of interest to see how closely his computed values agree with those chosen to fit the known phase boundaries. Upon choosing X_0 at 0.43, we find agreement is obtained by taking

(a) $U_\alpha(X_0) - U_\beta(X_0) = -0.016$ ev per atom, in contrast to Jones' value of 0,

(b) $U'_\alpha(X_0) - U'_\beta(X_0) = 0.21$ ev per atom, in contrast to Jones' value of 0.14,

(c) $U''(X_0) = 3.8$ ev per atom, in complete agreement with Jones' value. The value of the fourth unknown constant required by experiment is

$$\nu_\alpha/\nu_\beta = 1.10.$$

A plot of the phase boundaries according to Eqs. (12) and (13), and according to the above constants, is given in Fig. 1. The constants were chosen to give agreement with experiment above 500°C, which temperature is slightly above the critical temperature for ordering. By extending the $(\alpha+\beta)|\beta$ boundary below 500°C we see that it intersects the $\beta|(\beta+\alpha)$ boundary near 100°C. We conclude that the β -phase of brass would become unstable below 100°C were this phase not to become ordered.

In his early work Hume-Rothery demonstrated the approximate equivalence of the $\alpha|(\alpha+\beta)$ and $(\alpha+\beta)|\beta$ boundaries of different alloys provided the diagrams have as abscissa the electron-atom ratio n rather than atomic concentration X . An

identical equivalence would be given by Eqs. (12)–(16) if $U_\alpha(n) - U_\beta(n)$ were the same for all systems, as well as $U'_\alpha(n)$ and ν_α/ν_β . It is expected that small differences in the $T-n$ diagrams will arise as a result of small variations in these quantities. In the derivation of Eqs. (12)–(16) an assumption was introduced which, while apparently justified in the case of β -brass, may lead to appreciable error in other systems. This assumption was that $U''_\alpha(X)$ and $U''_\beta(X)$ were identical, and hence that $U'_\alpha(X) - U'_\beta(X)$ is independent of X over the region of interest. Now Jones has shown that this difference decreases with decreasing X , becoming zero at an electron-atom ratio of 1.25. As may be seen from Eqs. (12)–(13), the effect of this variation will be to decrease the width of the $(\alpha+\beta)$ region as this region moves to the left with increasing temperature, and simultaneously to increase the temperature variation of the center of this region. An indication of such effects may be found in the Cu-Ga and Ag-Zn systems.

3. ELASTIC ANISOTROPY

As was first pointed out by Webb,⁶ β -brass has the highest elastic anisotropy of any cubic metal so far examined, the ratio of $E_{[111]}/E_{[100]}$ at room temperature being 8.9. The elastic anisotropy is still greater when expressed in terms of the two shear coefficients C_{44} and $(C_{11} - C_{12})/2$. The first of these coefficients refers to a shear across the (100) plane in an arbitrary direction, the second to a shear across the (110) plane in the $[1\bar{1}0]$ direction. From the measurements of Good⁷ one finds that the ratio of these two shear coefficients varies from 18 at room temperature to 19 above the critical temperature for ordering.

A search for the origin of the high elastic anisotropy of β -brass may best start by a comparison of the shear elastic coefficients of α - and of β -brass, given in Table I. It is seen that in passing from the face-centered cubic to the body-centered cubic structure the C_{44} coefficient is more than doubled while the $(C_{11} - C_{12})/2$ coefficient is nearly halved.

The anomalously low value of the $(C_{11} - C_{12})/2$ shear coefficient of β -brass may readily be seen to be a direct consequence of the combination of

TABLE I. Shear elastic coefficients of α - and β -brass (in units of 10^{12} ergs/cm²).

Metal	C_{44}	$(C_{11} - C_{12})/2$
α -brass (f.c.c.)*	0.72	0.18
β -brass (b.c.c.)**	1.73	0.093

* f.c.c. = face centered cubic.

** b.c.c. = body centered cubic.

⁶ W. Webb, Phys. Rev. **55**, 297 (1939).

⁷ W. A. Good, Phys. Rev. **60**, 605 (1941).

a body-centered cubic lattice with ions containing only closed shells. Thus a body-centered cubic packing of balls manifests no resistance to a simple (110) $[\bar{1}10]$ shear. This lack of shear resistance is a consequence of the fact that such a shear leaves the distance between closest neighbors unchanged to a first approximation. In metals the resistance to shear arises primarily from two sources:⁸⁻¹⁰ (a) the exchange interaction between ions, (b) the electrostatic interaction between conduction electrons and ions. The first type of interaction may be regarded as acting only between closest neighbors, and in a body-centered cubic structure gives a positive contribution to $(C_{11}-C_{12})/2$ when the interaction is one of attraction, a negative contribution when it is repulsive, as is the case when the positive ions contain only closed shells. The second type of contribution, electrostatic interaction, gives a positive contribution which is independent of the ion structure. From the computations of Fuchs⁸ on copper, one sees that in a body-centered cubic copper lattice the negative contribution of the exchange interaction will more than compensate for the positive contribution of the electrostatic interaction, and that, therefore, in such a lattice $(C_{11}-C_{12})/2$ would be negative, i.e., the lattice would be mechanically unstable. The low value of this constant in β -brass may therefore be regarded as a manifestation of the tendency of the ion exchange interaction to render the body-centered cubic lattice mechanically unstable with respect to a (110) $[\bar{1}10]$ shear. It is therefore anticipated that all β -type alloys with closed inner shells will have a similarly low value of this shear constant.

The susceptibility of body-centered cubic structures to mechanical instability with respect to a (110) $[\bar{1}10]$ type shear furnishes an interpretation as to the limitations of body-centered cubic lattices to certain places in the periodic table. Aside from the alkali metals where the ions are too small to overlap to an appreciable extent, we would anticipate that no body-centered cubic lattices would be found in metals with completely or nearly completely closed shells. The other non-

⁸ K. Fuchs, Proc. Roy. Soc. [A]151, 585 (1935); 153, 622 (1936); 157, 444 (1936).

⁹ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford Press, 1936), pp. 147-150.

¹⁰ F. Seitz, reference 1, pp. 373-378.

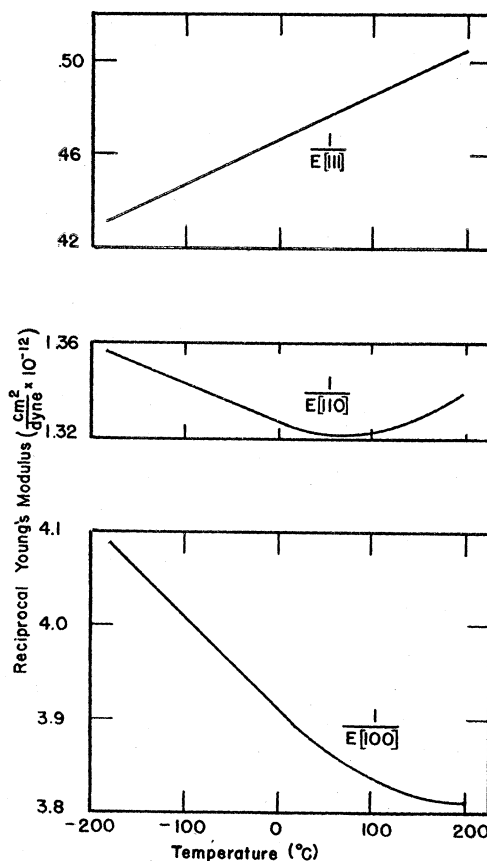


FIG. 4. Reciprocal Young's moduli of beta-brass, after Rinehart.

alkali body-centered cubic metals, V, Cr, Fe, Co, Mo, Ta, W, Eu, Th, Ba, have as free atoms from three to six electrons in the inner d shell, out of a possible maximum of ten, or (Eu) six f -electrons out of a possible maximum of fourteen, with the two exceptions Tl and Ba.

The high elastic anisotropy of β -brass is in part caused by the anomalously large value of the C_{44} shear constant. No satisfactory interpretation of this anomaly has been found.

4. ANOMALOUS TEMPERATURE COEFFICIENTS OF ELASTIC MODULI

In Fig. 4 are reproduced the observations of Rinehart¹¹ on the temperature variation of the reciprocal elastic moduli $E^{-1}_{[111]}$, $E^{-1}_{[110]}$, $E^{-1}_{[100]}$ of β -brass. Contrary to the normal behavior of reciprocal moduli, the last two decrease rather

¹¹ J. S. Rinehart, Phys. Rev. 58, 365 (1940); 59, 308 (1941).

than increase with a rise in temperature, i.e., a rise in temperature increases the elastic resistance of β -brass crystals with respect to tensile stresses along the $[110]$ and $[100]$ axes.

In order that a clue may be obtained as to the anomalous temperature variation shown in Fig. 4, we shall write the reciprocal tensile moduli in terms of the bulk modulus $(C_{11}+2C_{12})/3$ and the two shear coefficients C_{44} and $(C_{11}-C_{12})/2$.

$$\begin{aligned} E^{-1}_{[111]} &= (9K)^{-1} + (3C_{44})^{-1}, \\ E^{-1}_{[110]} &= (9K)^{-1} + (4C_{44})^{-1} + \{12(C_{11}-C_{12})/2\}^{-1}, \\ E^{-1}_{[100]} &= (9K)^{-1} + \{6(C_{11}-C_{12})/2\}^{-1}. \end{aligned}$$

From an inspection of these equations we see that the relative importance of the shear modulus $(C_{11}-C_{12})/2$ increases as we pass from $E_{[111]}$ through $E_{[110]}$ to $E_{[100]}$. Since this is the same order in which the temperature coefficient anomalously increases, we are led to suspect that the bulk modulus and the shear coefficient C_{44} have normal temperature coefficients, while only the shear coefficient $(C_{11}-C_{12})/2$ has an abnormal temperature variation.

As was seen in the previous section, in β -brass the shear coefficient $(C_{11}-C_{12})/2$ is the sum of two terms, a positive term arising from the electrostatic interaction of the conduction electrons and the positive ions, and a negative term arising from the repulsive exchange interaction of the positive ions. The positive term varies comparatively slowly with lattice constant a , namely as $1/a^4$. On the other hand, the negative term varies rapidly with the lattice parameter. The effect of thermal expansion *per se* is therefore to decrease the negative term more rapidly than the positive term, leading to a net increase in the shear constant $(C_{11}-C_{12})/2$. Before this interpretation of the anomalous temperature coefficient can be accepted, it is necessary to estimate the order of magnitude of the positive temperature coefficient of $(C_{11}-C_{12})/2$. On using the notation of Mott and Jones,⁹ we find the negative contribution to $(C_{11}-C_{12})/2$ to be proportional to $W'(r)$, where W is the exchange energy of two ions at a distance r . The temperature coefficient of this negative term is therefore $(rW''/W')\alpha$, where α is the

linear thermal expansion coefficient. On taking the values given by Mott and Jones for r^2W'' and rW' in the case of copper, we obtain the value of -17 for rW''/W' . Using the average value of 15×10^{-6} for copper¹² in the range -200°C to R.T. we obtain 2.5×10^{-4} as the temperature coefficient of the negative term in $(C_{11}-C_{12})/2$. This value is of the same order of magnitude as the temperature coefficient of $E_{[100]}$ in β -brass at low temperatures, which may be obtained from Fig. 4 as 1.7×10^{-4} . The change in sign of the temperature coefficient of $(C_{11}-C_{12})/2$ at about 200°C is caused by the decrease in the coefficient which is associated with disordering, a decrease which is apparent from the work of Good.⁷

The above interpretation of the anomalous temperature coefficients of the elastic moduli leads to an interesting prediction as to the influence of pressure upon the elastic shear coefficient $(C_{11}-C_{12})/2$ of β -brass. If thermal expansion increases $(C_{11}-C_{12})/2$, then we anticipate that contraction caused by pressure will decrease this constant. An elementary computation shows this decrease will be of the magnitude of several percent per 10^8 /atmospheres pressure.

The same anomaly in the temperature coefficient of $(C_{11}-C_{12})/2$ is to be expected in all β -phase alloys in which the positive ions have closed shells, as well as in the body-centered cubic element Ba and in the body-centered cubic phase of Tl. On the other hand, in the simple cubic lattices of the NaCl type the repulsive exchange interaction between adjacent ions tends to make the shear coefficient C_{44} negative. The same argument used above for β -brass would lead to the conclusion that in simple cubic lattices the temperature coefficient of C_{44} is positive, or at least only slightly negative. This is indeed the case. From the measurements of Rose,¹³ Durand,¹⁴ and Siegel¹⁵ we find that in NaCl and in KCl the temperature coefficient of C_{44} is only one-fifth that of $(C_{11}-C_{12})/2$.

¹² F. C. Nix and D. MacNair, Phys. Rev. **60**, 597 (1941).

¹³ F. C. Rose, Phys. Rev. **49**, 50 (1935).

¹⁴ M. A. Durand, Phys. Rev. **50**, 449 (1936).

¹⁵ S. Siegel, Phys. Rev. **61**, 84 (1942).