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# Second-, third-, and fourth-order elastic constants of $\beta$-brass*

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Complete sets of elastic constants of $\beta$-brass of two compositions are given. The fourth-order elastic constants are deduced from the temperature dependence of the second-order elastic constants. The elastic constants are explainable in terms of a Born-Mayer-type core exchange interaction between nearest and next-nearest neighbors. The next-nearest-neighbor contributions are greater than the nearest-neighbor contributions for $C_{111}$ and $C_{1111}$, and provide stability for the small shear constant $C' = (C_{11} - C_{12})/2$.

## I. INTRODUCTION

The Cauchy relations for the six third-order elastic constants (hereafter called TOEC) of cubic crystals are $C_{112} = C_{166}$ and $C_{123} = C_{144} = C_{456}$. For Cu, Ag, and Au, Hiki and Granato[1] found that (a) the TOEC tended to fit the Cauchy relations better than did the second-order elastic constants (SOEC), and (b) that $C_{112}$ was of the order of $\frac{1}{2}C_{111}$ while $C_{123}$ was of the order of zero. Since relation (b) follows for nearest-neighbor (nn) central-force interactions for the fcc lattice they interpreted their results to mean that the short-range exchange interaction between closed ion cores predominates for higher-order elastic constants.

For such materials (overlapping closed shells) the dominant factor determining the pattern of relations between the TOEC then becomes simply the geometric structure of the crystal. If this is so, then one would expect completely different patterns for different structures. For example, nearest-neighbor central-force interactions should give equal contributions to all six of the TOEC for the bcc and CsCl structure, and zero contributions to all but $C_{111}$ for the Sc and NaCl structure.[2,3]

To test this hypothesis measurements were made on $\beta$-brass with the CsCl structure. Two different compositions within the narrow $\beta$ range were used to look also for the relative influence of changes in conduction-electron densities.

The surprising result found is that all but $C_{111}$ do indeed follow approximately the expected nn relation, but that next-nearest neighbors (nnn) (which for $\beta$-brass follow the NaCl arrangement) contribute even more than do the nn contributions to $C_{111}$. The noncentral valence electronic effects are found to play a minor role in the TOEC pattern.

## II. EXPERIMENTAL

Two sets of $\beta$-brass crystals in the form of $15 \times 16 \times 17$-mm cubes were obtained. One set with an alloy concentration of 48.3 at.% zinc was purchased from Monocrystals, Inc. of Cleveland, Ohio. A second set with composition 44.4 at.% zinc was purchased from Aremco Products, Inc. of Briarcliff Manor, N.Y. The compositions of these crystals were determined after the ultrasonic measurements were finished by the Analytical Facilities Laboratory of the Materials Research Laboratory at Urbana, Illinois.

The SOEC were measured by the usual pulse-echo technique. Details of the experimental techniques as well as an extended discusssion and calculation of the directional dependence of the mode Grüneisen $\gamma$'s are given in the theses of Swartz[4] and Bensch.[5] The results are given in Table I together with the values obtained by McManus[6] and Lazarus.[7] The values reported by McManus and Lazarus correspond to 48-at.%-zinc and 50-at.%-zinc alloy concentrations, respectively. The results are in reasonable agreement.

The variation of the SOEC with temperature and stress was measured by using the two-specimen interferometric method developed by Hiki and Granato.[1] The coefficient of expansion used to make the transit time and density corrections was obtained from the data of Owen and Pickup.[8] The results for the temperature coefficients are shown in Table II. Values were obtained from the combinations of many measurements so that these temperature coefficients are overdetermined. The tabulated values are given by a least-squares analysis.

A representative plot of change in natural veloc-

TABLE I. Second-order adiabatic elastic constants of $\beta$-brass (units of $10^{12}$ dyn/cm$^2$).

| $C_{11}$ | $C'=\frac{1}{2}(C_{11}-C_{12})$ | $C_{44}$ | Composition |
|---|---|---|---|
| 1.258 ± (0.005) | 0.0855 ± (0.009) | 0.810 ± (0.004) | 44.3 at.% Zn |
| 1.241 ± (0.002) | 0.0995 ± (0.003) | 0.809 ± (0.001) | 48.3 at.% Zn |
| 1.24 | 0.079 | 0.795 | McManus (Ref. 6) 48 at.% Zn |
| 1.291 | 0.097 | 0.824 | Lazarus (Ref. 7) ~50 at.% Zn |

ity versus stress for uniaxial compression is shown in Fig. 1. The numbers on the curves correspond to the equations developed by Thurston and Brugger,[9] which relate the measured stress change of natural velocity to the TOEC.

Since the measurements overdetermined the TOEC, a least-squares program was adopted for the evaluation of these constants. In the evaluation of the results for the 48.3-at.%-zinc alloy the data for nine uniaxial compression measurements were given weighting equal to the data for five hydrostatic stress measurements. This was done because the scatter in the data for both uniaxial and hydrostatic results was about the same. In the evaluation of the results for the 44.3-at.%-zinc alloy, a weighting factor of 10 for the hydrostatic versus uniaxial data was adopted for the least-squares program since the scatter of these measurements was greater for the uniaxial measurements. The results of both sets of measurements are shown in Table III. The least-squares "error" that is quoted indicates the precision of the results, but does not take into account the possible systematic errors.

The hydrostatic-pressure derivatives of the SOEC determined from the five hydrostatic-stress measurements are tabulated in Table IV, where they may also be compared with earlier values given by Lazarus[7] for a composition of about 50 at.% Zn. There is approximate agreement. The source of the discrepancy between the values for the three compositions is not known, but it does not appear to be systematic with composition.

## III. DISCUSSION

### A. Short-range central potential

At first a simplified discussion will be given assuming that the third-order constants are dominated by a short-range closed-shell exchange interaction of the Born-Mayer type. This will be found to give a fair account of the observed TOEC with a potential which is rather close to that derived for Cu under similar approximations. A more complicated potential is then introduced to take account of conduction-electron effects, including Coulomb, Fermi, exchange, and correlation but neglecting band-structure effects. The electronic effects tend to cancel each other out. This helps to explain the relatively good account given by the exchange forces alone, while also providing a basis for a lattice-parameter calculation.

TABLE II. Temperature derivatives of SOEC (adiabatic) (units of $10^8$ dyn/cm$^2$ °C).

| $\frac{dC_{11}}{dT}$ | $\frac{dC'}{dT}$ | $\frac{dC_{44}}{dT}$ | $\frac{dB^S}{dT}$ | Composition |
|---|---|---|---|---|
| −2.34 ± (0.24) | 0.35 ± (0.12) | −4.12 ± (0.12) | −2.80 | 44.3 at.% Zn |
| −2.07 ± (0.13) | 0.09 ± (0.07) | −3.60 ± (0.22) | −2.23 | 48.3 at.% Zn |

The major result found in these measurements as given in Table III is that $C_{111}$ is about −12 and all the other TOEC are about −4 in units of $10^{12}$ dyn/cm$^2$ for both compositions. There are minor variations in this pattern, both for a given specimen and between the two specimens. This can be partly attributed to effects of conduction-electronic contributions, but is probably mostly within the experimental error.

As was intimated in the Introduction above, the repulsive exchange contribution to the TOEC from nearest neighbors should be the same for all six constants. The surprising result of the measurements was that $C_{111}$ was much larger than the other five constants. This suggests consideration of the next-nearest-neighbor (repulsive exchange) contribution to the TOEC. In $\beta$-brass the six next-nearest neighbors are only 15% farther apart than the eight nearest neighbors. This leads one to suppose that an nnn exchange contribution might be of considerable importance.

If the total energy per unit volume of a crystal is expressed as a sum of an additive short-range two-body central-force term due to the exchange interaction between closed shells, $U^c$, and the energy due to all other interactions, $U^e$, then

$$U=U^c+U^e=\frac{1}{2V_0}\sum W(r)+U^e(\eta_{ij}), \qquad (1)$$

where $V_0$ is the atomic volume, $W(r)$ is the energy per ion pair as a function of the ion-pair separation $r$, the sum is taken over ion pairs, and $\eta$ is the usual Lagrangian strain. The elastic constants are given by

$$C_{ijklmn\ldots}=\frac{\partial^n U}{\partial\eta_{ij}\,\partial\eta_{kl}\,\partial\eta_{mn\ldots}}, \qquad (2)$$

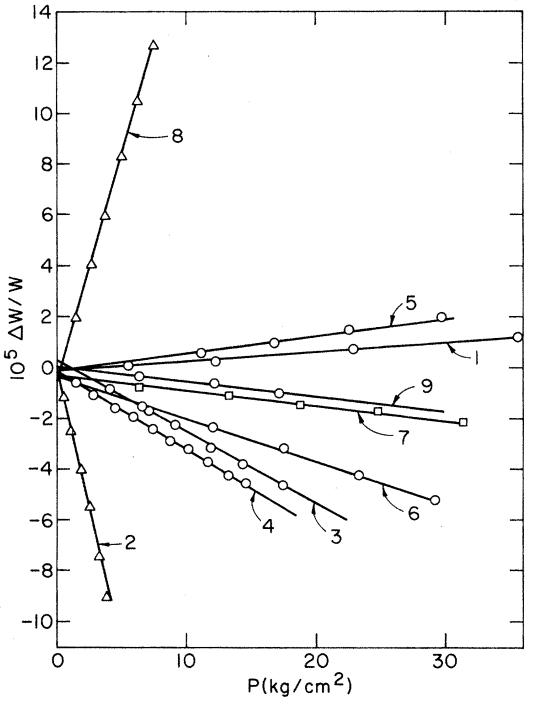

FIG. 1. Natural velocity change vs uniaxial stress for the 48.3-at.%-Zn alloy. Numbers correspond to the Thurston-Brugger numbering scheme for various applied stresses and sound-wave modes.

where $n$ represents the order of the elastic constant. The closed-shell repulsive contribution $C^c_{ijklmn\ldots}$ to the elastic constants are easily expressed in terms of derivatives of $W(r)$ using

$$r^2 - r_0^2 = 2\sum_{i,j} \xi_i \xi_j \eta_{ij} \tag{3}$$

for the difference in the square of the distance of a particle from the reference particle in the deformed and undeformed state,[2] where $\xi_i$ is the Cartesian coordinate of the particle in the undeformed state. Then

$$\frac{\partial}{\partial \eta_{ij}} = \xi_i \xi_j \frac{1}{r}\frac{d}{dr} = \xi_i \xi_j D \tag{4}$$

and

TABLE III. Third-order elastic constants (TOEC) of $\beta$-brass (units of $10^{12}$ dyn/cm²).

| | 44.3 at.% Zn alloy | 48.3 at.% Zn alloy |
|---|---|---|
| $C_{111}$ | −12.21 ± (0.34) | −12.52 ± (0.16) |
| $C_{112}$ | −5.11 ± (0.21) | −4.75 ± (0.13) |
| $C_{155}$ | −5.09 ± (0.17) | −3.96 ± (0.10) |
| $C_{123}$ | −4.40 ± (0.64) | −4.67 ± (0.15) |
| $C_{144}$ | −4.60 ± (0.25) | −3.85 ± (0.15) |
| $C_{456}$ | −2.69 ± (0.77) | −3.99 ± (0.16) |

TABLE IV. Hydrostatic-pressure derivatives.

| $\frac{\partial C_{11}}{\partial P}$ | $\frac{\partial C_{44}}{\partial P}$ | $\frac{\partial C'_L}{\partial P}$ | $\frac{\partial C'}{\partial P}$ | $\frac{\partial B^S}{\partial P}$ | Composition |
|---|---|---|---|---|---|
| 5.38 | 3.20 | 8.44 | 0.150 | 5.18 | 44.3 at.% Zn |
| 5.27 | 2.31 | 7.42 | 0.155 | 5.07 | 48.3 at.% Zn |
| | 3.17 | | 0.23 | 4.44 | Lazarus (Ref. 7) |

$$\begin{aligned}
C^c_{11} &= \frac{1}{2V_0}\sum \xi_1^4 [D^2 W(r)]_{r=r_0}\,,\\
C^c_{12} &= \frac{1}{2V_0}\sum \xi_1^2 \xi_2^2 [D^2 W(r)]_{r=r_0}\,,\\
C^c_{111} &= \frac{1}{2V_0}\sum \xi_1^6 [D^3 W(r)]_{r=r_0}\,,\\
C^c_{112} &= \frac{1}{2V_0}\sum \xi_1^4 \xi_2^2 [D^2 W(r)]_{r=r_0}\,,\\
C^c_{123} &= \frac{1}{2V_0}\sum \xi_1^2 \xi_2^2 \xi_3^2 [D^3 W(r)]_{r=r_0}\,,
\end{aligned} \tag{5}$$

where the Cauchy relations $C^c_{12} = C^c_{44}$, $C^c_{112} = C^c_{166}$, $C^c_{123} = C^c_{144} = C^c_{456}$ hold, with similar relations for higher orders. The summation is to be taken over all neighbors of the ion at the origin, in principle, but usually only extends to first- or second-nearest neighbors for potentials which fall off rapidly with distance. These equations hold for the static lattice, since no effects of temperature are explicitly included.

In the $\beta$-brass structure, the Cartesian coordinates of the eight nn are given by

$$|\xi_1| = |\xi_2| = |\xi_3| = \tfrac{1}{2} a_0\,, \tag{6}$$

where $a_0$ is the cubic-lattice cell dimension. For each of the six nnn, two of the coordinates are zero, while the third has magnitude $a_0$. Thus one would obtain a pattern for the exchange contribution to the TOEC when nn and nnn contributions are considered of the form shown in Eqs. (7),

$$\begin{aligned}
C^c_{111} &= \frac{4}{V_0}\frac{a_0^6}{2^6}[D^3 W(r)]_{r=a_0\sqrt{3}/2} + \frac{1}{V_0} a_0^6 [D^3 W(r)]_{r=a_0}\,,\\
C^c_{112} &= C^c_{123} = C^c_{144} = C^c_{166} = C^c_{456}\\
&= \frac{4}{V_0}\frac{a_0^6}{2^6}[D^3 W(r)]_{r=a_0\sqrt{3}/2} = C^0_{111}\,.
\end{aligned} \tag{7}$$

It may be observed that the pattern of the TOEC predicted by use of the exchange contributions only is reasonably well followed by the TOEC for both alloy compositions. The TOEC for $\beta$-brass come closer to agreeing with the Cauchy relations than do those for the noble metals.

The simplest assumptions which can be made in a further analysis are that (i) the exchange interactions have the Born-Mayer form,

$$W(r) = A\exp\{-[B(r/r_0 - 1)]\}\,, \tag{8}$$

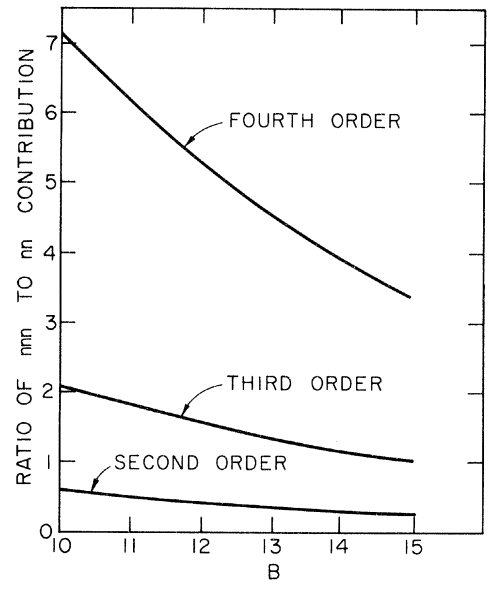

FIG. 2. Ratio of the next-nearest-neighbor to the nearest-neighbor contribution to $C_{11}$, $C_{111}$, and $C_{1111}$ for $\beta$-brass as a function of the Born-Mayer hardness parameter $B$.

where $A$ is the energy per ion pair, $B$ is a hardness parameter, and $r_0 = (\frac{1}{2}\sqrt{3})\, a_0$ is the equilibrium nn distance, and that (ii) the same potential holds for the Cu-Cu, Cu-Zn, and Zn-Zn interactions. There are then only two parameters introduced, $A$ and $B$, which can be fitted to the two values found for the third-order elastic constants. From this, the fourth-order elastic constants are then determined, which are compared later with those deduced from the temperature dependence of the SOEC. The comparison is found to be close, justifying assumption (ii) that all these interactions are comparable. The exchange contributions to the TOEC then become

$$C^c_{111} = -\left(C^0_{111} + \frac{AB}{V_0}\left(2\sqrt{3} + 4B + \tfrac{8}{9}\sqrt{3}\,B^2\right) e^{-0.155B}\right),$$

where (9)

$$C^0_{111} = -\left(\frac{AB}{V_0}\left(\tfrac{4}{9} + \tfrac{4}{9}B + \tfrac{4}{27}B^2\right)\right) \text{ with } V_0 = \frac{4}{3\sqrt{3}}\, r_0^3 .$$

Only $C^c_{111}$ has contributions from the nnn. In order to see what effect this nnn interaction has on $C_{111}$, the ratio given by

$$y = \frac{C^{\text{nnm}}_{111}}{C^{\text{nn}}_{111}} = \frac{9\sqrt{3} + 18B + 4\sqrt{3}\,B^2}{2 + 2B + (2/3)B^2}\, e^{-0.155B} \tag{10}$$

is plotted in Fig. 2. The corresponding ratios for the second- and fourth-order elastic constants are also shown in Fig. 2. One can see that, for reasonable values of $B$ ($10 \le B \le 15$), the nnn contribution to $C_{111}$ is quite appreciable and, in fact, is larger than the nn contribution. Also, the relative influence of the nnn contribution increases with the order of the elastic constants.

The hardness parameter $B$ obtained from the ratio of $C_{111}$ to the average of the other five TOEC is 11. If $B$ is made larger and the value of $C_{111}$ is held fixed, the value of $C^0_{111}$ becomes larger. The value of $B$ which gives $C^0_{111}$ equal to the largest of the small TOEC (for the 48.3-at.%-Zn alloy) is $B = 12.6$. The value $B = 11$ is smaller than the value of $B = 12.6$ which was reported by Hiki, Thomas, and Granato[10] for Cu. This difference is small but the impact on the value of $C_{111}$ is appreciable since $B$ appears in the exponential function for the nnn contribution. When the value of $B = 11$ is inserted into Eq. (9), the value of $A$ obtained from the experimentally observed $C_{111}$ is $A = 0.138$ eV/(ion pair).

In a cubic crystal there are eleven nonzero fourth-order elastic constants.[11] For only nn and nnn central-force interactions, there are then only two "independent" fourth-order elastic constants:

$$C_{1111},\quad C_{1112} = C_{1122} = C_{1155} = C_{1266} = C_{4444} = C_{1123} = C_{1144}$$
$$= C_{1255} = C_{1456} = C_{1455} = C^0_{1111} . \tag{11}$$

When the formalism for calculation of the TOEC from the exchange-interaction contribution is extended to fourth-order elastic constants, one obtains

$$C_{1111} = (AB/V_0)\left[\left(\tfrac{20}{27} + \tfrac{20}{27}B + \tfrac{8}{27}B^2 + \tfrac{4}{81}B^3\right) + \left(10\sqrt{3} + 20B + \tfrac{16}{3}\sqrt{3}\,B^2 + \tfrac{16}{9}B^3\right) e^{-0.155B}\right], \tag{12}$$

$$C^0_{1111} = (AB/V_0)\left(\tfrac{20}{27} + \tfrac{20}{27}B + \tfrac{8}{27}B^2 + \tfrac{4}{81}B^3\right) .$$

For the values of $A$ and $B$ determined from the TOEC in Eqs. (12), the fourth-order constants become $C_{1111} = 150 \times 10^{12}$ dyn/cm² and $C^0_{1111} = 21 \times 10^{12}$ dyn/cm². These are next compared with values deduced from the temperature dependence of the SOEC.

Using Brugger's formulation, Hiki, Thomas, and Granato[10] have developed an expression for the temperature derivatives of the isothermal SOEC at constant volume in terms of the tensor Grüneisen parameter and the second-, third-, and fourth-order elastic constants. The calculation gives

$$\left.\frac{\partial C^T_{\alpha\beta\delta\xi}}{\partial T}\right|_V = -\rho_0 k \sum_j \left.\frac{\partial \gamma_j^{\alpha\beta}}{\partial \eta_{\gamma\xi}}\right|_T ,$$

where

$$\left.\frac{\partial \gamma_j^{\alpha\beta}}{\partial \eta_{\delta\xi}}\right|_T = 2\gamma_j^{\alpha\beta}\gamma_j^{\delta\xi} - \frac{N_m N_n}{2W_j}\left(C_{\alpha\beta\gamma\xi mn} + 4C_{\alpha\beta mun}\delta U_u U_\xi + C_{\alpha\beta\gamma\xi mun\,v} U_n U_v\right) . \tag{13}$$

Here $\rho_0$ is the density of the crystal, $k$ is Boltzmann's constant, $\gamma_j$ is the mode Grüneisen parameter, $N_j$ is the propagation direction, $U_j$ is the polarization, $W_j$ is the mode velocity, and the summation is over all normal modes.

When the appropriate summations in Eq. (13) are carried out for $\partial C_{11}^T/\partial T$, $\partial C_{12}^T/\partial T$, and $\partial C_{44}/\partial T$, the equations can be solved for the constants $C_{1111}$ and $C_{1111}^0$. The values obtained are $C_{1111}=156\times 10^{12}$ dyn/cm$^2$ and $C_{1111}^0=24\times 10^{12}$ dyn/cm$^2$. Since there are three independent SOEC temperature coefficients the two fourth-order constants should have been overdetermined. It turns out that the difference between $\partial C_{44}/\partial T$ and the terms not involving the fourth-order constants on the right-hand side of Eq. (13) is small, so that variations in these two factors lead to rather large variations in the derived fourth-order constants. However, the results obtained for the values of $C_{1111}$ and $C_{1111}^0$ from $\partial C_{11}^T/\partial T$ and $\partial C_{12}^T/\partial T$ when substituted into the $\partial C_{44}/\partial T$ relationship give consistent results within experimental error.

The values of the fourth-order elastic constants deduced from the experimental temperature dependence of the SOEC are in excellent agreement with those calculated using the Born-Mayer parameters deduced by fitting the TOEC. This would not be so if, for example, the Zn-Zn and Cu-Cu interactions were greatly different from the Cu-Zn interactions, and the agreement justifies the simplifying assumption used here in obtaining the Born-Mayer parameters. It should be noted that the influence of the nnn interactions is even more pronounced in fourth order than in third order. The strong influence of nnn interactions is accounted for by the fact that the nnn atoms are only 15% father away than the nn atoms and a longitudinal displacement of atoms in a $\langle 100\rangle$ direction forces the nnn atoms into direct contact. It thus appears that the major features of the third- and fourth-order constants can be simply understood in terms of only two Born-Mayer parameters.

The Born-Mayer parameters derived above contrast strongly with those used by Gilat and Dolling[12] in fitting their neutron-scattering measurements. Their hardness parameter $B$ for the nearest-neighbor interaction is 29.3, or almost three times larger than that found here. There is no way to obtain the observed pattern of third- and fourth-order elastic constants found here with this value of $B$. Also, they report a large difference between the second-nearest-neighbor Cu-Cu and Zn-Zn forces.

Using the same potential, the second-order elastic constants can be calculated as well. These are given, together with the third- and fourth-order elastic constants, in the second column of Table V. The experimental values are given in the last column. The computed closed-shell overlap contributions $C^c$ give a remarkably good fit (within about 20%) to the second-order constants as well.

### B. Long-range contributions

The agreement found for the elastic constants using only a two-parameter short-range central force encourages us to consider longer-range forces to (a) test the assumption made that short-range forces dominate the higher-order elastic constants, (b) provide for lattice stability and calculate a lattice parameter, and (c) see if conduction-electron effects account for the remaining small differences between the two alloy compositions. This can be done simply with a free-electron

TABLE V. Contributions to the second-, third-, and fourth-order elastic constants of $\beta$-brass in units of $10^{12}$ dyn/cm$^2$. The ion-core overlap contribution ($C^c$) is fitted with the Born-Mayer parameters of $B=11$ and $A=0.138$ eV. Next-nearest-neighbor ion-core overlap effects contribute to $C_{11}$, $C_{111}$, and $C_{1111}$, but not to the remaining constants. The electrostatic ($C^{es}$), Fermi ($C^F$), and exchange ($C^x$) contributions are computed using $Z_A(\mathrm{Cu})=1$ and $Z_B(\mathrm{Zn})=2$. The values in parentheses are for effective charges of 66%. For $C_{\alpha\beta\gamma}^{\mathrm{expt}}$, the average of the results in Table III are listed. For $C_{\alpha\beta}^{\mathrm{tot}}$, the small correlation contributions given in the text have been included.

| | $C^c$ | $C^{es}$ | $C^F$ | $C^x$ | $C^{\mathrm{tot}}$ | $C^{\mathrm{expt}}$ |
|---|---|---|---|---|---|---|
| $C_{11}$ | 1.572 | −1.708(−0.744) | 1.770(0.885) | −0.776(−0.446) | 0.802(1.211) | 1.24 |
| $C_{12}$ | 1.020 | −0.486(−0.212) | 0.443(0.222) | −0.109(−0.062) | 0.865(0.965) | 1.04 |
| $C_{44}$ | 1.020 | −0.486(−0.212) | 0.664(0.332) | −0.328(−0.189) | 0.844(0.925) | 0.81 |
| $C_{111}$ | −12.52 | 5.16(2.25) | −8.26(−4.13) | 3.32(1.91) | −12.3(−12.49) | −12.4 |
| $C_{112}$ | −4.42 | 1.69(0.74) | −1.18(−0.59) | 0.26(0.15) | −3.65(−4.12) | −4.9 |
| $C_{155}$ | −4.42 | 1.69(0.74) | −1.77(−0.89) | 0.77(0.44) | −3.73(−4.13) | −4.5 |
| $C_{123}$ | −4.42 | −0.95(−0.41) | −0.30(−0.15) | 0.04(0.02) | −5.63(−4.96) | −4.5 |
| $C_{144}$ | −4.42 | −0.95(−0.41) | −0.44(−0.22) | 0.11(0.06) | −5.70(−4.99) | −4.2 |
| $C_{456}$ | −4.42 | −0.95(−0.41) | −0.66(−0.33) | 0.33(0.19) | −5.70(−4.97) | −3.3 |
| $C_{1111}$ | 150 | | | | 150 | 156 |
| $C_{1111}^0$ | 21 | | | | 21 | 24 |

model.

We then approximate $U^e$ in Eq. (1) by

$$U^e = U^{es} + U^{fe}, \tag{14}$$

where $U^{es}$ is the electrostatic and $U^{fe}$ is the free-electron energy.

The electrostatic energy for a cubic metal with a $\beta$-brass structure may be written[13] as a linear contribution of a term for the CsCl structure and one for a bcc structure:

$$U^{es} = \tfrac{1}{4} U^{bcc}(Z_A + Z_B)^2 + \tfrac{1}{4} U^{CsCl}(Z_A - Z_B)^2, \tag{15}$$

where $U^{bcc}$ and $U^{CsCl}$ are the electrostatic energies per unit volume for the body-centered (metallic) and cesium-chloride structure, $Z_A$ is the effective charge of the copper ions, and $Z_B$ is the effective charge of the zinc ions. Using the tabulated values given by Fuller and Naimon[14] with the observed lattice constant of $a = 2.94$ Å, the elastic constants given in Table V are obtained for $Z_A = 1$ and $Z_B = 2$. These are not small compared to the closed-shell short-range terms for second order, but tend to become relatively smaller for higher order.

The free-electron contributions are treated as in the work of Suzuki *et al.*[15] Thus we have terms in the energy per unit volume as shown below:

$$U^{fe} = \left\{ \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} - \frac{3 k_F e^2}{4\pi} + \frac{e^2}{2a_0} \left[ -0.115 + 0.031 \ln\left(\frac{r_s}{a_0}\right) \right] \right\} n_0, \tag{16}$$

where $k_F$ is the Fermi wave vector, $a_0$ the radius of the first Bohr orbit of hydrogen, $r_s$ the "radius" of the ion, and $n_0$ the density of electrons, i.e., $n_0 = (Z_A + Z_B)/a^3$. Each of these terms can be treated as being volume dependent in the formulation of the Brugger elastic constants and expressed in the form

$$U = P v^n, \tag{17}$$

where $v = V/V_0$ and $V_0$ is the equilibrium volume. Using Eq. (16), one obtains $P^F = 0.1596 \times 10^{12}(Z_A + Z_B)^{5/3}$ dyn/cm$^2$, $n^F = -\frac{2}{3}$, $P^x = -0.2275 \times 10^{12}(Z_A + Z_B)^{4/3}$ dyn/cm$^2$, $n^x = -\frac{1}{3}$, $P^{cor} = -0.226 \times 10^{12}(Z_A + Z_B)$ dyn/cm$^2$, and $n^{cor} = -0.117$.

With these values, the elastic constants calculted by using the results given in Table I of Suzuki *et al.*[15] for $Z_A = 1$, $Z_B = 2$ are given in Table V. The correlation contributions for $C_{11}$, $C_{12}$, $C_{44}$ are $-0.056$, $-0.003$, and $-0.026$, respectively, in units of $10^{12}$ dyn/cm$^2$, and have been omitted as separate entries in the table, but have been included in the total ($C_{\alpha\beta}^{tot}$).

The free-electron contributions tend to cancel the electrostatic contributions. This explains the remarkable agreement obtained earlier using only the short-range forces. A similar cancellation was found to occur for copper and silver by Thomas,[16] who included band-structure effects, but calculated Fuchs rather than Brugger elastic constants defined by Eq. (2).[15,17,18]

The changes resulting from the inclusion of the long-range forces with $Z_A(\mathrm{Cu}) = 1$ and $Z_B(\mathrm{Zn}) = 2$ do not improve the over-all agreement between the calculated ($C^{tot}$) and the experimental ($C^{expt}$) elastic constants. More important, equilibrium ($dU/dv = 0$) is not obtained at the observed lattice constant. If it is supposed that the conduction-electronic charge is not uniformly distributed, so that a part of the charge effectively shields the ion cores, then one may introduce a parameter $f$ giving the fraction of the charge which is uniformly distributed. The value which gives equilibrium at the observed lattice spacing using Eqs. (15) and (17) is $f = 0.66$. With this value of $f$, the conduction-electron effects are reduced and are shown in parentheses in Table V. For this choice of $f$, the calculated elastic constants of all orders are in good agreement with the experimental ones. It is to be noted that only three parameters ($A$, $B$, and $f$) have been used to fit 12 constants (the lattice parameter, three second-order constants, six third-order constants, and two fourth-order constants). For $f = 0.66$, the contributions to the energy $U^c$, $U^{es}$, $U^F$, $U^x$, and $U^{cor}$ are 0.079, $-1.168$, 0.498, $-0.566$, and $-0.448$, respectively, in units of $10^{12}$ erg/cm$^3$ for a total binding energy of $-1.605 \times 10^{12}$ erg/cm$^3$, or $-12.7$ eV/ion.

The volume-dependent terms in the free-electron approximation are insufficient to provide the observed Cauchy-relation failure ($C_{12} - C_{44}$) in second order. Further noncentral terms are needed, which may be supposed to lie in the neglected band-structure effects. The nnn closed-shell overlap term plays a strong role in stabilizing the small shear constant $C' = \frac{1}{2}(C_{11} - C_{12})$ as anticipated by McManus.[6] The variations found between the five smaller third-order elastic constants do not correlate with the calculated conduction-electron effects. However, systematic errors in these results may be of the same order as the variations, and more accurate results would be needed to assess the influence of band-structure effects on the third-order elastic constants.

## IV. SUMMARY

The pattern found for the third-order elastic constants of $\beta$-brass can be explained by assuming short-range central nearest- and next-nearest-neighbor forces. Using the same assumptions, the temperature dependence of the second-order elastic constants can be analyzed to obtain the fourth-order elastic constants. The resulting fit to the six third-order and 11 fourth-order constants then implies that the Cu-Cu, Cu-Zn, and Zn-Zn interactions are approximately the same, so that only a two-parameter Born-Mayer potential is needed. The resulting hardness parameter $B$ of 11 is in fair agreement with the value of 12.6 found by Hiki and Granato for the Cu-Cu interaction by analyzing the third- and fourth-order elastic constants of Cu, but is in disagreement with the results found by Gilat and Dolling in analyzing their neutron-scattering results in $\beta$-brass.

The next-nearest-neighbor effects are found to be larger than the nearest-neighbor effects for $C_{111}$ and $C_{1111}$. This is because longitudinal displacements along the cubic axes displace next-nearest-neighbor atoms, which are separated only 15% more than are nearest neighbors, directly along a line between the next-nearest-neighbor atoms.

Long-range conduction-electron effects calculated for $Z(\mathrm{Cu}) = 1$ and $Z(\mathrm{Zn}) = 2$ do not account for the observed lattice parameter and do not improve the fit to the elastic constants. If it is supposed that a part of the charge effectively shields the ion cores, then the effective charge (about two-thirds) required to give the observed lattice parameter also improves the agreement between the calculated and observed SOEC, while having relatively little effect on the TOEC.

The principal result obtained in the analysis is that next-nearest-neighbor interactions dominate the nonlinear elastic behavior, and also provide stability of the lattice for the $C' = \frac{1}{2}(C_{11} - C_{12})$-type shears.

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