Table 5. The potential constants and the calculated values of elastic constants for α phase Ag–Cd alloys

$X_{\scriptscriptstyle B}$	D (eV)	r ₀ (Å)	α (1/Å)	C ₁₁ calcu	C ₁₂ lated	C ₁₁ experi	C ₁₂ mental
0.00	0.3178	3.0887	1.4340	1.334	0.887	1.240	0.934
1.29	0.3155	3.0913	1.4321	1.321	0.878	1.228	0.925
1.84	0.3135	3.0951	1.4254	1.305	0.869	1.216	0.913

Elastic constants: 1012 dyn/cm2 unit.

Helmholtz free energy F is given by

$$F = E(a) + 3NkT \cdot \log(1 - e^{-\Theta_D/T})$$
$$- NkT \cdot D\left(\frac{\Theta_D}{T}\right), \tag{6}$$

where Θ_D is the Debye temperature and D(x) is the well known Debye function. Using this expression, the equation of state, or P-V relation, and Grüneisen parameters were calculated and published in our previous paper[12]. The quasi-chemical approach assuming only constant nearest neighbor interactions cannot lead a P-V relation but our fairly simple method could do it. However, it should be noted that the phenomena associated with atomic rearrangement such as solute clustering can not be treated by the present method. The empirical Morse function is useful in applying some types of problems for metallic solid solutions but its validity is limited because of the lack of sound physical basis.

Acknowledgments—The authors are grateful to Prof. R. R. Hasiguti for his continuous interest and encouragements. This work is partially supported by the International Copper Research Corporation.

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ELASTIC CONSTANTS AND THEIR PRESSURE DERIVATIVES OF α -BRASS SINGLE CRYSTALS

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(Received 21 March 1973; in revised form 26 September 1973)

Few elastic constant measurements on α -brass single crystals are reported in recent literature[1,2]. Although Subrahmanyam and Krishnamurty[3] have conducted extensive measurements on polycrystalline alloys, their results, when converted to the equivalent single crystal parameters by the Kneer equations[4], show considerable scatter in the data.

The present note reports the values of ultrasonically measured elastic constants and their pressure derivatives for copper and two α -brass single crystals (19 at.% Zn and 29 at.% Zn). The elastic constants, expressed in terms of the Youngs modulus (*E*), the adiabatic bulk modulus (*B_s*), and the shear constant *C*₁₁ are in good agreement with the previous single crystal data, showing a nearly linear decrease of the three parameters with zinc concentration. The data obtained on polycrystalline samples by Subrahmanyam and Krishnamurty[3] for the bulk modulus scatters around the values obtained from single crystal measurements, while the *C*₁₁ and *E* values show, apart from the scatter, a more systematic deviation (see Figs. 1–3).

The crystals used for the measurements were purchased from Monocrystals Inc. of Cleveland, Ohio. Both crystals were homogenized by annealing for more than 100 h at temperatures up to 690°C and furnace cooled. The lattice parameters corresponding to these compositions are 3.658 Å (19% Zn) and 3.681 Å (29% Zn)[5]. The crystals were oriented by Laue X-ray back reflection and cut to expose two parallel (110) faces to within 1° of this orientation and lapped flat and paralleled to within one part in 10^5 . The length of the crystals along the direction of sound wave propagation was 1.25_5 cm and 1.73_7 cm for the 19 and 29% Zn crystals respectively.

For each crystal the velocities of the longitudinal and the two transverse waves were measured by the well known McSkimin pulse superposition method[6] using 10 MHz X and Y cut quartz transducers.

The pressure derivatives of the elastic moduli were determined by measuring the ultrasonic wave velocities as a function of pressure up to 100,000 psi. The ultrasonic wave velocities were found to be linear functions of the pressure over this range. Further details of the experimental procedure are discussed in Ref. [7].

The results of the measurements are summarized in Table 1. As has been discussed previously [8] the errors implicit in the measurement of elastic constants in alloy single crystals are much smaller than the unresolvable uncertainties in the absolute composition values (assumed here as $\pm 1\%$). The irregular behaviour of the pressure derivatives of the elastic constants near the phase boundary (i.e. at 29% Zn) is similar to that observed for random Cu–Au alloys at the ordering composition[8].

The composition dependence of the elastic constants was also calculated, using some necessary simplifying assumptions, by means of the Electron Cell model, which has been used with fairly good success for representing



Fig. 1. Bulk modulus as function of composition.



Fig. 2. Shear constant as function of composition.



Fig. 3. Young's modulus as function of composition.

Table 1.

Alloy (Zn/Cu)	0.0/1.0	0.19/0.81	0.29/0.71
a (Å)	3.6147	3.658	3.681
$C (10^{12} dyn/cm^2)$	0.755	0.737	0.719
$C' (10^{12} \text{dyn/cm}^2)$	0.235	0.189	0.191
B_{s} (10 ¹² dyn/cm ²)	1.374	1.33,	1.26_{6}
$B_{\rm T}$ (10 ¹² dyn/cm ²)	1.346	1.29_{2}	1.21_{8}
$\partial C/\partial P$	2.37	2.37	2.4,
$\partial C' / \partial P$	0.592	0.47_{7}	0.52_{0}
$\partial B_s / \partial P$	5.84	5.73	7.65

 $C = C_{44}, C' = 0.5 (C_{11} - C_{12}), B_s = (C_{11} + 2C_{12})/3$

the equation of state of the noble metals [9] and the elastic and cohesive properties of Cu–Au alloys [8].

As is discussed in Ref. [9] the cohesive energy of the noble metals may be expressed in the form

$$\epsilon_{\rm coh} = \frac{A}{r_s^3} + \frac{F}{r_s^2} + \frac{B}{r_s} + \epsilon_{\rm corr} + 6\,\epsilon_p$$

where

$$\epsilon_p = D(-\alpha d) - Cd^6. \tag{1b}$$

In the above equations A, F, B, D, α and C are characteristic constants determinable for each of the noble metals; r_s and d are the Wigner–Seitz cell radius and the interatomic distance, respectively, ϵ_{corr} the correlation energy and, ϵ_p the pairwise interaction energy.

The contributions to the shear constants can be separated, into the parts corresponding to electrostatic interactions and pairwise interactions (according to the Fuch's equations [10]) and a contribution from the distortion of the Fermi surface. The bulk modulus, on the other hand, is proportional to the second derivative of the cohesive energy with respect to volume.

The elastic constants for the Cu–Zn alloys were calculated on the basis of the following assumptions:

(a) The contributions to the elastic constants from electron cell and electrostatic interactions were calculated on the basis of an average electron density of $(1 + x_{zn})$ electrons/cell with a corresponding average positive charge on each ion. It was assumed, as would correspond to a free electron model, that the electron cell constants *A*, *B* and *G* vary with $n^{1/3}$ and *F* with $n^{2/3}$, where *n* is the average number of conduction electrons/atom. (e.g. see Ref. [10]).

(b) The constants of the repulsive part of the pairwise potential were assumed to be the same as those for copper, since the configuration of the closed electron shells is likely to be very similar for the two ions.

(c) The Van der Waals interaction constant *C* for zinc was determined from polarizabilities estimated from Pauling's "Mole Refraction" constants [12], as has been done previously for the noble metals [13], $(C_{cu} = 57.6 \text{ kcal } \text{Å}^6/\text{gr. at}, C_{zn} = 50.3 \text{ kcal } \text{Å}^6/\text{gr. at.})$

(d) The contribution from Fermi surface distortion to the shear moduli was assumed constant and equal to that determined (by difference between experimental and calculated values of shear moduli) for copper[9].

The elastic moduli so calculated are compared to the experimental values in Table 2, and the corresponding values of C_{11} , B_s and E (calculated by the Kneer equations) have been traced in Figs. 1–3. In view of the approximations made, the agreement of calculated and experimental data seems satisfactory. The excessive decrease of the calculated bulk modulus with composition possibly indicates that the approximation relative to the changes of the electron cell constants with composition is the least adequate. On the other hand, the better agreement of calculated and experimental shear moduli suggests that the Born-Mayer potential between zinc and copper atoms is not, in fact, very different from that between copper ions.

This is further support for a previously suggested conclusion[10] that the Born–Mayer potentials calculated from elastic and cohesive properties, after subtracting the

Table 2. Calculated and experimental elastic moduli (in 10^{12} dyn/cm^2)

Alloy (Zn/Cu):	0.05/0.95	0.10/0.90	0.19/0.81	0.29/0.71
C_{44}^{P}	0.848	0.810	0.754	0.692
C_{44}^{e}	0.292	0.315	0.361	0.414
C_{44}^{f}	-0.378	-0.378	-0.378	-0.378
C_{44} (calc)	0.762	0.747	0.737	0.728
C_{44} (exp)	0.742†		0.737	0.719
C'^p	0.248	0.238	0.222	0.205
C'^{e}	0.031	0.034	0.038	0.044
C''	-0.034	-0.034	-0.034	-0.034
C' (calc)	0.245	0.238	0.226	0.215
C' (exp)	0.221†		0.189	0.191
B_s (calc)	1.348	1.287	1.224	1.161
B_s (exp)	1.339†		1.339	1.266

†95.41%Cu-4.59%Zn. Ref.[2].

electron effects, may be physically more realistic, and applicable to a broader range of problems.

Acknowledgements—The financial support of the Center for Material Research of the University of Maryland received for the realization of this project is gratefully acknowledged.

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