bate ionic pseudopotentials was studied using first-order perturbation theory (see Sec. II A and Ref. 25), showed $\Phi_{\min}$ to decrease by only ~0.05 eV from the value found in Sec. II C.

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# Elastic Constants of α-Phase Cu-Al Alloys*

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The three independent adiabatic elastic constants and their temperature derivatives have been measured near room temperature for single-crystal α-phase Cu-Al alloys for compositions to 13 at.% Al using an ultrasonic pulse-superposition technique. The elastic shear constant $C_{44}$ increases linearly over this entire composition range. The elastic shear coefficient $C' = \frac{1}{2}(C_{11} - C_{12})$ decreases linearly with increasing Al content to approximately 7 at.% Al. For higher Al concentrations $C'$ decreases at a greater rate. The measured bulk modulus $B = \frac{1}{3}(C_{11} + 2C_{12})$ decreases in a linear manner with increasing Al concentration. The temperature derivatives of the elastic constants are only weakly dependent upon alloy composition. The change in the Debye temperature $\Theta_0$ calculated from the elastic data is positive and in agreement with that determined calorimetrically. The changes in the elastic constants upon alloying have been corrected for the effects of lattice expansion. The corrected change in the bulk modulus $B$ upon alloying is positive. The corrected changes in the elastic shear coefficients extrapolated to 0°K have been analyzed in terms of a generalized Fuchs theory of homogeneous deformation. It is concluded that a conduction-electron term must be considered in calculating the shear coefficients of copper along with the original electrostatic and ion-core repulsion terms, and that changes in this conduction-electron term with increasing Al content make a significant contribution to the changes in the elastic shear coefficients upon alloying. The results indicate an increase in conduction-electron density with increasing Al concentration.

## I. INTRODUCTION

The elastic constants of a single-crystal binary alloy provide information on the interatomic forces in the alloy and their dependence on solute concentration. By comparing the measured elastic constants with those calculated from atomic models, the relative contributions to the interatomic forces of the several terms in the lattice energy can be estimated. In addition, the elastic constants are useful in the investigation of mechanical and thermal properties such as phase stability, solid-solution strengthening, and dynamic dislocation phenomena.

We have measured the second-order elastic constants of the α-phase copper-aluminum alloy system as a function of temperature and solute concentration. The α–Cu-Al system is of interest for several reasons. Recently, long-range high-velocity dislocation propagation has been observed in α–Cu-Al single crystals deformed in tension.[1,2] Knowledge of the interatomic forces in the alloy is basic to the understanding of these phenomena. Not unrelated is the fact that it is possible to grow very nearly perfect single crystals over a wide range of the α phase. This is discussed in more detail below. In addition, because of the large valence difference between copper and aluminum and the wide range of stability of the α phase (to 20 at.% Al), a significant variation in the electron per atom ratio can be obtained. Thus, it should be possible to investigate the effect of variation of valence-electron density on the interatomic forces.

Coherent inelastic neutron-scattering measurements have been completed on two single-crystal α–Cu-Al alloys with solute concentrations of 4.1 and 10.0 at.% Al.[3] A local mode was observed in both specimens at a frequency which was in good agreement with that predicted by simple mass-defect theory. However, the observed changes in the frequencies of the in-band modes could not be predicted by mass-defect theory. It was concluded that changes in the interatomic forces must be important.

The elastic constants of several α-phase copper alloy systems have been measured previously. Smith and co-workers measured the elastic constants of Cu-Ni[4] and Cu-Zn, -Ga, -Ge, -Al, and -Si.[5] Only two compositions of the α–Cu-Al system were included. Bacon and Smith[6] measured the elastic constants of an analogous silver-based alloy series. These measurements were all at room temperature. Rayne[7] measured the composition dependence of the elastic constants of α–Cu-Zn from 4.2 to 300 °K. Waldorf[8] completed similar measurements for the Cu-Mn system.

Each of these investigations included a comparison of the measured elastic shear coefficients to those calculated from atomic models. This is a productive form of analysis for elastic-constant data of metals and alloys. Shear coefficients, which relate to strictly volume conserving deformations, are emphasized because they do not depend on terms in the lattice energy which are functions of atomic volume only.

It is generally accepted that the most important lattice energy contributions to the elastic shear coefficients of copper are the electrostatic energy, the exchange interaction energy of nearest-neighbor ion cores, and the total (Fermi) energy of the conduction electrons. The original calculation of the elastic shear coefficients of copper by Fuchs[9] omitted the conduction-electron contribution. This was based on the assumption of a spherical Fermi surface for monovalent copper. It is now well known that the Fermi surface of copper intersects the $\{111\}$ faces of the Brillouin zone, and several attempts have been made to calculate the Fermi-energy contribution to the elastic shear coefficients.[10,11] However, there is still no generally accepted decomposition of the elastic constants of copper.

An extension of the Fuchs model was developed to interpret the early copper alloy elastic-constant data.[4,5] The Fermi energy was not included. The first attempt[7,8] to include a Fermi-energy contribution to the elastic shear coefficients was based on the zone overlap model developed by Jones[12] for $\beta$–Cu-Zn. It is now understood that this is not applicable to $\alpha$-phase alloys.

The only theoretical calculation of the change in the Fermi-energy contribution to the elastic shear coefficients of $\alpha$-phase copper alloys is that of Collins.[11] He developed a rigid-band calculation based on the cone model of Ziman[13] and expressed in terms of measured Fermi-surface parameters. Although Collins found poor agreement between measured and calculated shear constants of copper and silver alloys, this could have been due to his neglect of changes in the ion-core contribution. The changes in the elastic shear coefficients of the $\alpha$–Cu-Al alloy system presented here are in qualitative agreement with the calculation of Collins.

## II. EXPERIMENTAL PROCEDURE

The $\alpha$-phase of the Cu-Al binary alloy system is stable to approximately 20 at.% Al. Over most of this range the separation of the liquidus and solidus lines of the phase diagram is very small.[14] This minimizes the concentration gradient during solidification and allows the growth of very nearly perfect alloy single crystals. The crystals have little substructure and low dislocation densities within the subgrains.[15] As one indication of this, the ultrasonic attenuation was very low for all the crystals prepared for this investigation. Typically, several hundred echoes could be observed.

The alloys were prepared by casting together 99.999% pure copper and spectroscopically pure aluminum in graphite molds at a pressure of $10^{-7}$ Torr. The casting process was repeated for each alloy to ensure a homogeneous mixture. Single crystals were grown from oriented 4-mm square cross-section seeds in variable cross-section split graphite molds. The crystals had $[001]$ growth axes and either 10- or 15-mm square cross section with $\{110\}$ surfaces. The crystals were grown at a rate of 1 in./h and at a pressure of $10^{-7}$ Torr. They were allowed to cool slowly before removal from the mold. A small graphite lineage filter was inserted in the seed compartment to prevent the direct propagation of dislocations from the seed into the crystal.

The orientation of each crystal was checked by the Laue backreflection x-ray technique. All but three crystals were within 1° of the desired orientation. The maximum misorientation was 2°. For the three crystals misoriented by more than 1°, the measured elastic constants were subsequently corrected to the appropriate pure mode value. Specimens were spark-cut from the single-crystal boules, and opposite faces were spark-planed flat and parallel for ultrasonic propagation. Finally, all alloy specimens, except one with 0.75 at.% Al, were annealed at high vacuum for 100 h at 800 °C and then slowly cooled to room temperature.

The densities $\rho$ of the alloy specimens were determined by hydrostatic weighing. The compositions were then determined using the measured densities and the x-ray lattice-parameter data of Obinata and Wasserman.[16] Their data for lattice parameter vs solute concentration is linear over the entire $\alpha$ phase. The solute concentrations, lattice parameters, and densities for the alloy crystals used in this investigation are summarized in Table I.

Ultrasonic waves were generated by 10-MHz $X$- and $AC$-cut quartz transducers attached to the alloy crystals with heated Nonaq stopcock grease. The wave velocities were measured by the McSkimin pulse-superposition technique.[17] In this method, the repetition rate of an rf pulse is matched to an integral multiple $p$ of the round-trip transit time $t$ of the specimen-transducer system. The true round-trip transit time $\delta$ for the specimen can be determined from the relation

$$\delta = t/p + \gamma/360f - n/pf \quad . \tag{1}$$

Here $n$ is an integer, $f$ is the rf frequency, and $\gamma$ is a measure of the phase shift at the specimen-

TABLE I. Solute concentrations, lattice parameters, and densities of the α–Cu-Al alloy crystals used in this investigation.

| at.% Al | Lattice parameter (Å) | Density (g cm$^{-3}$) |
|---|---|---|
| 0 | 3.6147 | 8.9384 |
| 0.75 | 3.6171 | 8.8862 |
| 3.4 | 3.6240 | 8.7048 |
| 4.85 | 3.6277 | 8.6047 |
| 6.9 | 3.6331 | 8.4605 |
| 7.5 | 3.6347 | 8.4197 |
| 8.4 | 3.6370 | 8.3591 |
| 10.3 | 3.6419 | 8.2275 |
| 13.25 | 3.6495 | 8.0222 |

bond interface. From measurements at two different frequencies, the resonant frequency of the transducer and one differing by several percent, the $n = 0$ overlap condition and the phase shift correction can be determined. All measurements were taken with $p = 1$, which maximized the sensitivity for setting the overlap condition. For the low-attenuation alloy crystals, sound-velocity changes of 5 ppm could be detected.

The ultrasonic wave velocities were measured over a temperature range of approximately 0–30 °C. The temperature was determined by means of a chromel-constantan thermocouple, which had been calibrated against a platinum resistance thermometer, attached directly to the specimen. Before each measurement, the temperature of the specimen was held constant to better than 0.01 °C for at least 10 min. A typical plot of the pulse repetition frequency $t^{-1}$ vs temperature is shown in Fig. 1.

## III. EXPERIMENTAL RESULTS

The quantity actually determined as a function of temperature in these experiments is the true transit time $\delta$; the path length is determined at one temperature, but its temperature dependence is unknown. Therefore, the measurements are analyzed in terms of a natural velocity $W = l_0/\delta$ and its temperature derivative $(\partial W/\partial T)$ with the path length $l_0$ normalized to 20 °C.

### A. Elastic Constants

The orientation of our specimens allowed measurement of four different ultrasonic wave velocities and, hence, the corresponding adiabatic elastic coefficients $\rho W^2$. The four wave velocities correspond to the elastic coefficients $C_{11}$, $\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$, $C_{44}$, and $\frac{1}{2}(C_{11} - C_{12})$. We have four measurements of the three second-order elastic constants of a cubic crystal. A least-squares analysis was used to compute the most probable values of the three independent elastic constants and the probable error. This error is a measure of the consistency of the measurements and represents errors in the transit time, path length, and orientation.

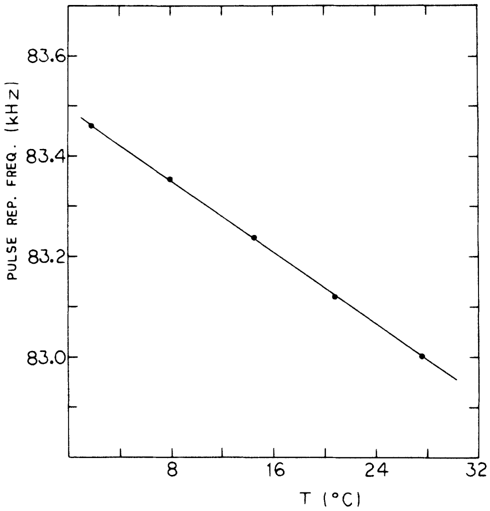

FIG. 1. Typical plot of the pulse repetition frequency $t^{-1}$ vs temperature.

A summary of the adiabatic elastic constants of the α–Cu-Al alloy system normalized to 20 °C is presented in Table II. In addition to the elastic constants $C_{11}$, $C_{12}$, and $C_{44}$, Table II includes entries for the shear coefficient $C' = \frac{1}{2}(C_{11} - C_{12})$ and the bulk modulus $B = \frac{1}{3}(C_{11} + 2C_{12})$. For $C_{11}$, $C_{44}$, and $C'$, the probable error is always less than 0.001 $\times 10^{12}$ dyn cm$^{-2}$. For $C_{12}$ and $B$, the probable error is always less than $0.002 \times 10^{12}$ dyn cm$^{-2}$. Also included in Table II are the elastic constants of copper at 20 °C measured by Overton and Gaffney[18] and the elastic constants of the α–Cu-Al alloy system measured by Neighbours and Smith.[5] The unusual behavior of the measured values of $C_{44}$ of Neighbours and Smith is unexplained.

### B. Temperature Derivatives

The temperature derivatives at constant pres-

TABLE II. Adiabatic elastic-constants of the α–Cu-Al alloy system at 20 °C in units of $10^{12}$ dyn cm$^{-2}$.

| at.% Al | $C_{11}$ | $C_{12}$ | $C_{44}$ | $C' = \frac{1}{2}(C_{11} - C_{12})$ | $B = \frac{1}{3}(C_{11} + 2C_{12})$ |
|---|---|---|---|---|---|
| 0[a] | 1.692 | 1.219 | 0.754 | 0.237 | 1.377 |
| 0[b] | 1.687 | 1.216 | 0.756 | 0.236 | 1.372 |
| 0.75 | 1.690 | 1.220 | 0.761 | 0.235 | 1.376 |
| 3.4 | 1.676 | 1.215 | 0.764 | 0.230 | 1.369 |
| 4.85 | 1.667 | 1.215 | 0.767 | 0.226 | 1.366 |
| 6.9 | 1.657 | 1.209 | 0.773 | 0.224 | 1.358 |
| 7.5 | 1.649 | 1.207 | 0.774 | 0.221 | 1.354 |
| 8.4 | 1.641 | 1.208 | 0.775 | 0.217 | 1.352 |
| 10.3 | 1.626 | 1.204 | 0.780 | 0.211 | 1.344 |
| 13.25 | 1.594 | 1.197 | 0.788 | 0.199 | 1.330 |
| 4.81[c] | 1.658 | 1.216 | 0.749 | 0.221 | 1.363 |
| 9.98[c] | 1.595 | 1.176 | 0.766 | 0.209 | 1.316 |

[a] This experiment. [b] Reference 18. [c] Reference 5.

sure of the second-order elastic constants can be obtained from the relation

$$\frac{\partial C}{\partial T}=C\left(\frac{2}{W}\frac{\partial W}{\partial T}-\alpha\right). \qquad (2)$$

Here $\alpha$ is the coefficient of linear thermal expansion. We have used the value of $\alpha$ for copper at 20 °C ($\alpha=0.166\times10^{-4}\,°\mathrm{C}^{-1}$)[19] throughout. We know of no measurement of $\alpha$ for the Cu-Al alloy system. Although we expect $\alpha$ to vary with alloy composition, the changes in $\alpha$ should be small, and $\alpha$ itself is small compared to the first term in Eq. (2). Again, we have four measurements of the three independent elastic-constant temperature derivatives and, hence, can determine the most probable values and the probable errors. A summary of the temperature derivatives of the elastic constants of the $\alpha$–Cu-Al alloy system at 20 °C is presented in Table III. The probable errors are also included.

The elastic-constant temperature derivatives compiled in Table III depend only weakly on alloy composition. Variations between adjacent compositions are nearly equal to the probable error. In addition, the variations are not always monotonic. The largest systematic change occurs for $(\partial C'/\partial T)$. The weak dependence of the elastic-constant temperature derivatives on alloy composition is in agreement with the findings of Rayne[7] for Cu-Zn and Waldorf[8] for Cu-Mn.

The major exception to these statements is the significant change in $(\partial C_{44}/\partial T)$ and $(\partial C'/\partial T)$ between our values for pure copper and the lowest composition alloy specimen. It seems unlikely that this is an elastic effect representing a change in the character of the interatomic forces. Rather, we recall that it has been demonstrated that mobile dislocations can make a non-negligible contribution to the elastic constants of pure metals.[20] For an alloy, dislocations are certainly strongly pinned and would not affect the elastic constants. We suggest that the abrupt changes in the temperature derivatives indicate a temperature-dependent dislocation contribution to the elastic shear coefficients of the pure copper. In support of this we note that the copper specimen used in this work was prepared from 99.999% material and the shear-wave attenuation was significantly greater than that of the alloys. Further, we note the poor consistency of the measured temperature derivatives for pure copper. The probable errors for the pure copper temperature derivatives are much larger than for any of the alloys. This would be the result if dislocations made different fractional contributions to the different elastic modes. Also included in Table III are the temperature derivatives for pure copper of Overton and Gaffney[18] calculated from their tabulated data for $T\geqslant 260\,°\mathrm{K}$. The agreement with our measured values is within the probable error except for $(\partial C_{12}/\partial T)$ and $(\partial B/\partial T)$ which, in any case, must be computed as a difference of comparable numbers. It is possible that Overton and Gaffney's data also include a dislocation contribution. A consistency check is not available for their data since they measured only three elastic coefficients as a function of temperature.

### C. Extrapolation to 0°K

A principal objective of this investigation is to interpret the composition dependence of the elastic constants of the $\alpha$–Cu-Al alloy system. The analysis will be based upon the method of homogeneous deformation which treats the crystal as an anisotropic continuum. Hence, we wish to compare calculated elastic constants to those which would be measured in the absence of thermal and zero-point vibrations. To obtain such values we must extrapolate the elastic constants measured at high temperatures linearly to 0 °K.[21] This was done for the $\alpha$–Cu-Al system using the tabulated elastic constants and temperature derivatives. The results are presented in terms of the fractional change in the extrapolated elastic constants vs alloy composi-

TABLE III. Temperature derivatives of the elastic constants of the $\alpha$-Cu-Al alloy system at 20 °C in units of $10^8\ \mathrm{dyn\,cm^{-2}\,°C^{-1}}$.

| at.% Al | $\frac{\partial C_{11}}{\partial T}$ | $\frac{\partial C_{12}}{\partial T}$ | $\frac{\partial C_{44}}{\partial T}$ | $\frac{\partial C'}{\partial T}$ | $\frac{\partial B}{\partial T}$ |
|---|---|---|---|---|---|
| 0[a] | −3.60 ± 0.09 | −1.39 ± 0.16 | −2.82 ± 0.07 | −1.11 ± 0.09 | −2.13 ± 0.12 |
| 0[b] | −3.58 | −1.58 | −2.88 | −1.03 | −2.25 |
| 0.75 | −3.68 ± 0.01 | −1.60 ± 0.03 | −2.54 ± 0.01 | −1.04 ± 0.01 | −2.29 ± 0.02 |
| 3.4 | −3.54 ± 0.02 | −1.50 ± 0.04 | −2.53 ± 0.02 | −1.02 ± 0.02 | −2.18 ± 0.03 |
| 4.85 | −3.53 ± 0.03 | −1.50 ± 0.05 | −2.52 ± 0.02 | −1.01 ± 0.03 | −2.18 ± 0.03 |
| 6.9 | −3.47 ± 0.04 | −1.50 ± 0.06 | −2.53 ± 0.04 | −1.00 ± 0.04 | −2.14 ± 0.06 |
| 7.5 | −3.52 ± 0.02 | −1.53 ± 0.03 | −2.51 ± 0.02 | −1.00 ± 0.02 | −2.19 ± 0.02 |
| 8.4 | −3.46 ± 0.03 | −1.58 ± 0.06 | −2.51 ± 0.03 | −0.94 ± 0.03 | −2.21 ± 0.05 |
| 10.3 | −3.47 ± 0.01 | −1.55 ± 0.01 | −2.51 ± 0.01 | −0.96 ± 0.01 | −2.19 ± 0.01 |
| 13.25 | −3.36 ± 0.01 | −1.51 ± 0.03 | −2.49 ± 0.01 | −0.93 ± 0.01 | −2.13 ± 0.02 |

[a] This experiment.

[b] Reference 18.

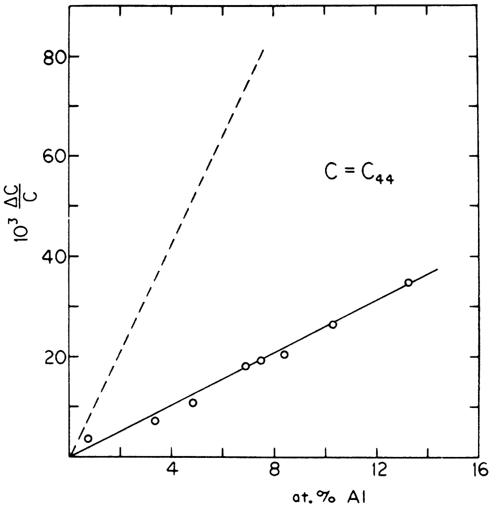

FIG. 2. Fractional change in the elastic shear coefficient $C = C_{44}$ of α–Cu-Al extrapolated to 0 °K. Dashed line represents the change that would be observed upon alloying at constant volume.

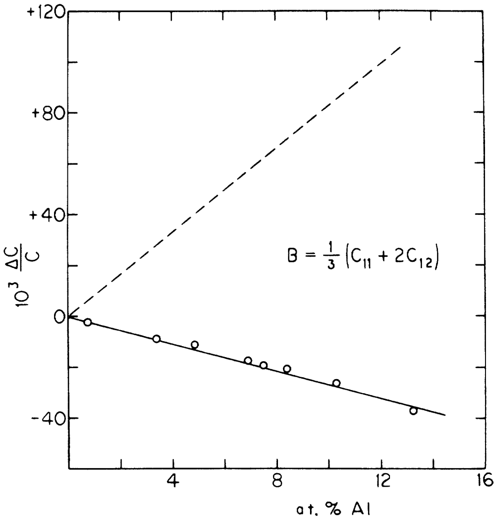

FIG. 4. Fractional change in the bulk modulus $B = \frac{1}{3}(C_{11} + 2C_{12})$ of α–Cu-Al extrapolated to 0 °K. Dashed line represents the change that would be observed upon alloying at constant volume.

tion. Results for the fractional change in the elastic coefficients $C = C_{44}$, $C' = (\frac{1}{2})(C_{11} - C_{12})$, and $B = (\frac{1}{3})(C_{11} + 2C_{12})$ are presented in Figs. 2–4, respectively. Since we question the measured temperature derivatives for copper, the extrapolated copper elastic constants are not used as a reference for the fractional changes. Rather, these are based on an intercept determined by assuming the linear dependence of the elastic constants on alloy composition discussed below.

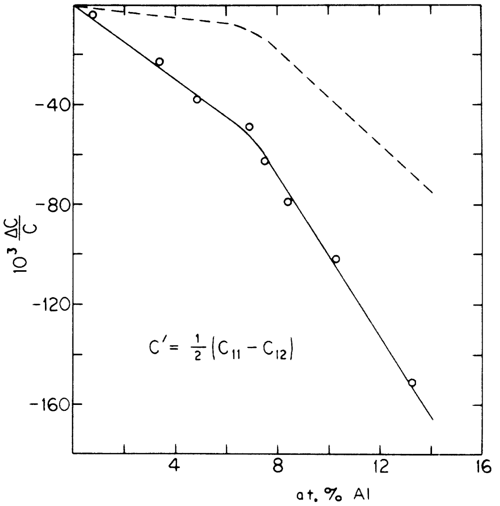

FIG. 3. Fractional change in the elastic shear coefficient $C' = \frac{1}{2}(C_{11} - C_{12})$ of α–Cu-Al extrapolated to 0 °K. Data have been fit with two straight lines to illustrate the greater rate of decrease of $C'$ above 7 at.% Al. Dashed line represents the change that would be observed upon alloying at constant volume.

Because of the weak dependence of the temperature derivatives of the elastic constants on composition, the qualitative features of the change in the elastic constants with alloy composition are the same for the measured values at room temperature and those extrapolated to 0 °K. The elastic constant $C_{44}$ (Fig. 2) increases in an apparent linear manner over the entire composition range investigated. This increase is a distinct feature of the composition dependence of the α-Cu-Al elastic constants. All other copper alloy systems with solute valence greater than one have shown a decrease in the measured value of $C_{44}$. The measured elastic shear coefficient $C' = (\frac{1}{2})(C_{11} - C_{12})$ (Fig. 3) decreases linearly to approximately 7 at.% Al. At higher compositions $C'$ decreases at a significantly greater rate. In Fig. 3, we have fit the results for $C'$ with two straight lines to illustrate this behavior. The fractional change in $C'$ is the largest measured; this has been noted for several other copper alloy systems.[5] The measured value of the bulk modulus $B = (\frac{1}{3})(C_{11} + 2C_{12})$ (Fig. 4) also decreases in an apparent linear manner over the entire composition range investigated.

### D. Correction to Constant Volume

The change in the elastic constants upon alloying can be considered to arise from two separate effects: (i) the change due to lattice expansion and (ii) the explicit change due to the addition of the solute $(\partial C/\partial x)_a$. The two effects can be separated from knowledge of the pressure derivatives of the

TABLE IV. Correction of the measured changes in the elastic coefficients of α–Cu-Al to those which would be observed upon alloying at constant volume. See Eq. (3) in the text.

| | $B=\frac{1}{3}(C_{11}+2C_{12})$ | $C=C_{44}$ | $C'=\frac{1}{2}(C_{11}-C_{12})$ |
|---|---|---|---|
| $B_T$[a] | 1.332 | 1.332 | 1.332 |
| $\left(\frac{\partial C}{\partial P}\right)_{x=0}$[b] | 5.59 | 2.35 | 0.58 |
| $\frac{d(\ln a)}{dx}$[c] | 7.14 | 7.14 | 7.14 |
| $3B_T\left(\frac{\partial C}{\partial P}\right)_{x=0}\left(\frac{d(\ln a)}{dx}\right)$[d] | 1.59 | 0.67 | 0.17 |
| $\frac{dC}{dx}$[d] | −0.40 | 0.22 | −0.20[e]<br>−0.42[f] |
| $\left(\frac{\partial C}{\partial x}\right)_a$[d] | 1.19 | 0.89 | −0.03[e]<br>−0.26[f] |

[a] Reference 18, units of $10^{12}$ dyn cm$^{-2}$.
[b] Reference 22.
[c] Reference 16, units of $10^{-4}$/at.% Al.
[d] Units of $10^{10}$ dyn cm$^{-2}$/at.% Al.
[e] For solute concentrations < 7 at.% Al.
[f] For solute concentrations > 7 at.% Al.

elastic constants of the solvent:

$$\left(\frac{\partial C}{\partial x}\right)_a=\frac{dC}{dx}+3B_T\left(\frac{\partial C}{\partial P}\right)_{x=0}\frac{d(\ln a)}{dx} . \tag{3}$$

The values of $(\partial C/\partial x)_a$ for the elastic coefficients $C_{44}$, $C'$, and $B$ are summarized in Table IV. The values of $(dC/dx)$, the total derivatives of the measured elastic constants, are taken from a straight-line fit to the extrapolated elastic constants (Figs. 2–4). In Eq. (3), $[d(\ln a)/dx]$ is the logarithmic derivative of the lattice parameter with respect to solute concentration, $B_T$ is the isothermal bulk modulus of copper, and $(\partial C/\partial P)_{x=0}$ is the hydrostatic pressure derivative of the elastic constant of copper. In Table IV, the pressure derivatives are taken from the work of Daniels and Smith.[22] Other determinations of the pressure derivatives are available, both at room temperature[23] and at low temperature.[24] But these involve measurements of the changes in the sound velocity with applied uniaxial stress and might contain a dislocation contribution. For consistency, room-temperature values are used for all three factors in the second term in Eq. (3). In fact, a low-temperature value for $[d(\ln a)/dx]$ is not available.

The fractional changes in the extrapolated elastic coefficients at constant volume are also indicated in Figs. 2–4 by the dashed lines. It is apparent that the correction to constant volume is an important effect. The fractional increase in $C_{44}$ at constant volume is a factor of 4 larger than the measured increase. The fractional change in $C'$ is still negative, but is very small compared to the measured change up to approximately 7 at.% Al. At higher concentrations it increases significantly. The fractional change in the bulk modulus at constant volume is positive as opposed to the negative change in the measured value.

### E. Short-Range Order

It has been hypothesized[25,26] that there is short-range order (SRO) of aluminum atoms in the α–Cu-Al alloy system for solute concentrations greater than 6 at.% Al.[27] The amount of SRO is dependent upon the thermal history of the specimen. Slow cooling of an annealed specimen through the temperature range 225–300 °C should maximize the SRO.[25] Hence, we must expect that several of our high-concentration alloy specimens are ordered.

If this is the case, the observation that the composition dependence of $C'$ changes markedly near the composition threshold for SRO suggests that the onset of SRO might contribute to this change. However, it is possible to explain the observed composition dependence of the elastic shear coefficients without reference to SRO. This is discussed further in Sec. VI.

One further comment can be made at this point. Preliminary measurements by one of us[28] of the elastic constants of the 8.4, 10.3, and 13.25 at.% Al alloy specimens were completed for both the as-grown and annealed states using a direct, unrectified pulse-echo technique. No differences in the elastic constants outside an experimental uncertainty of 0.2% were observed.

## IV. DEBYE TEMPERATURE

The 0 °K elastic constants can be used to calculate the 0 °K Debye temperature $\Theta_0$. This value $(\Theta_0)$ should agree with that determined from the low-temperature lattice specific heat. Agreement for several isoelectronic noble metal alloys has been summarized by Collins.[11] Veal and Rayne[29] found very close agreement for α–Cu-Zn.

For cubic solids, the calculation of $\Theta_0$ from the elastic constants can be accomplished rapidly using the formula given by deLaunay[30]:

$$\Theta_0=\left(\frac{9}{4\pi\Omega}\right)^{1/3}\left(\frac{h}{k}\right)\left(\frac{C_{44}}{\rho}\right)^{1/2}\left[\frac{9}{18+\sqrt{3}}\,f\left(\frac{s,t}{t_m}\right)\right]^{1/3}, \tag{4}$$

$$s=\frac{C_{11}-C_{44}}{C_{12}+C_{44}},\quad t=\frac{C_{12}-C_{44}}{C_{44}},\quad t_m=\frac{2s}{1-s} .$$

Here $\Omega$ is the atomic volume and $f$ is a function tabulated by deLaunay. We have used Eq. (4) to calculate the change in $\Theta_0$ for the α–Cu-Al alloy system with increasing solute concentration $(d\Theta_0/dx)$. The changes in density and atomic volume are taken from the lattice-parameter data of Obinata and Wasserman[16] summarized in Table I. The changes

TABLE V. Change in the Debye temperature $\Theta_0$ with increasing solute concentration for the $\alpha$–Cu-Al alloy system in units of °K/at.% Al.

| | $\frac{d\Theta_0}{dx}$ |
|---|---|
| Elastic data | |
| This experiment | 0.69 |
| Calorimetric data | |
| Zrudsky *et al.*[a] | 0.62 |
| Wu[b] | 0.50 |

[a] Reference 31. [b] Reference 32.

in the elastic constants are taken as the measured changes extrapolated to 0 °K. There should be a negligible difference between these changes and those measured at 0 °K. The derivatives of $f(s, t/t_m)$ were computed from a linear interpolation of deLaunay's tables. We find that the Debye temperature $\Theta_0$ increases with solute concentration. The value of $(d\Theta_0/dx)$ for solute concentrations less than 7 at.% is presented in Table V. Above 7 at.%, $\Theta_0$ still increases but at a slower rate.

The Debye temperature for the $\alpha$–Cu-Al alloy system has been determined calorimetrically by Zrudsky *et al.*[31] and by Wu.[32] We have calculated values of $(d\Theta_0/dx)$ from a least-squares fit to their results for aluminum concentrations less than 7 at.% Al. In each case this includes two alloy compositions in addition to copper. These values of $(d\Theta_0/dx)$ are also presented in Table V. The agreement is very satisfactory. Each calorimetric investigation included one specimen with aluminum concentration greater than 7 at.%. In each case the value of $\Theta_0$ deviated from the straight line determined by the other compositions. The deviation for a 10.0% specimen of Zrudsky *et al.* was in the direction consistent with our calculations (a less rapid increase in $\Theta_0$). The deviation for an 8.8% specimen of Wu was in the opposite direction. The substantial agreement between the elastic and calorimetric increase of $\Theta_0$ for low aluminum concentrations lends support to both the specific-heat and elastic-constant measurements.

## V. INTERPRETATION

The changes in all the elastic constants of the $\alpha$–Cu-Al alloy system with increasing Al concentration are linear up to approximately 7 at.% Al. In the analysis of this section we will limit the discussion to this portion of the $\alpha$ phase. We will comment on the results for higher Al composition in Sec. VI. Also, we will concentrate on the calculation of the elastic shear coefficients.

In the theory of homogeneous deformation, the elastic shear coefficients can be calculated as the second derivatives of the lattice energy with respect to appropriate shear strain parameters. Fuchs[9] constructed two shear deformations for which the volume was strictly conserved. One of these, describing an expansion of the lattice along a $\langle 100\rangle$ direction and contraction in the plane perpendicular to the $\langle 100\rangle$ direction, is related directly to the elastic shear coefficient $C' = \frac{1}{2}(C_{11} - C_{12})$. The second, describing an expansion of the lattice along a $\langle 111\rangle$ direction and contraction in the plane perpendicular to that, is related directly to the shear coefficient $C = C_{44}$.

### A. Previous Theory

For copper, the total lattice energy per atom can be written as

$$U = U_0 + U_E + U_R + U_F \ . \tag{5}$$

Here $U_0$ is the total energy of the lowest conduction-electron state, $U_E$ is the electrostatic energy, $U_R$ is the exchange energy between ion cores, and $U_F$ is the Fermi energy of the conduction electrons. In the original calculations of Fuchs,[9] it was assumed that only the terms $U_E$ and $U_R$ would be changed by a volume conserving shear deformation. For the fcc structure, the contributions of the term $U_E$ to the elastic shear coefficients are given by

$$\begin{aligned} C_E &= 0.9478\ (2e^2/a^4)\ , \\ C_E' &= 0.1058\ (2e^2/a^4)\ , \end{aligned} \tag{6}$$

where $a$ is the lattice parameter. Assuming nearest-neighbor interactions only, the contributions of the term $U_R$ are given by

$$\begin{aligned} C_R &= (4/a^3)\,(\tfrac{3}{4}\sqrt{2}\,aW_R' + \tfrac{1}{4}a^2W_R'')\ , \\ C_R' &= (4/a^3)\,(\tfrac{7}{8}\sqrt{2}\,aW_R' + \tfrac{1}{8}a^2W_R'')\ , \end{aligned} \tag{7}$$

where $W_R$ is the repulsive energy of a single ion pair, and the primes denote differentiation with respect to the interatomic distance.

The first attempts[4–6] to interpret the elastic constants of copper alloy systems used an extension of Fuchs's results for pure copper. Since the electrostatic contribution to the elastic shear coefficients [Eq. (6)] contains a charge squared, it was assumed that, for the alloys, this term would be multiplied by the square of an effective valence $Z = 1 + qx$. The change in the ion-core contribution [Eq. (7)] was assumed to be directly proportional to the number of modified ion interaction pairs. The proportionality constant is denoted by $\alpha$. For solutes with ion cores larger than copper, $\alpha$ should be positive; for solutes with ion cores smaller than copper, $\alpha$ should be negative. Hence, for low concentrations, the changes in the elastic shear coefficients upon alloying are given by

$$\left(\frac{\partial C}{\partial x}\right)_a = 2qC_E + \alpha\, C_R \ ,$$

$$\left(\frac{\partial C'}{\partial x}\right)_a = 2qC_E' + \alpha C_R' . \tag{8}$$

Here $C_E$, $C_E'$ and $C_R$, $C_R'$ are the electrostatic and ion-core contributions to the elastic shear coefficients of copper. $C_E$ and $C_E'$ are assumed to be well known, and $C_R$ and $C_R'$ are determined by subtraction of $C_E$ and $C_E'$ from the measured constants.

Values were obtained for $q$ and $\alpha$ for the several copper alloy systems mentioned previously. In all cases, $q$ was approximately equal to the excess valence $(Z-1)$ of the solute. As expected, $\alpha$ was negative for solute ion cores smaller than copper and positive for those larger. We have reexamined these measurements by assuming a linear fit to the experimental data and using Eqs. (3) and (8). In each case, we find a value of $q$ slightly larger than the excess valence of the solute. If we apply this analysis to the $\alpha$–Cu-Al elastic constants measured here, we obtain $q = 2.9$ and $\alpha = -0.8$. The value of $\alpha$ is similar to that obtained by Neighbours and Smith.[5] The value of $q$ is significantly greater than the excess valence of 2 for aluminum. Experimental values of $q$ greater than excess solute valence cannot be explained physically. This result is inconsistent with all theories of alloy charge distribution. This leads us to look for a third contribution to the alloy elastic shear coefficients.

### B. Fermi-Energy Contribution

Since the Fermi surface of copper intersects the Brillouin zone, the Fermi energy $U_F$ must contribute to the elastic shear coefficients. We denote these contributions by $C_F$, $C_F'$. Assuming that $C_E$, $C_E'$ are well known, we have, effectively, two relations for the four unknowns $C_R$, $C_R'$ and $C_F$, $C_F'$. The problem is to determine a reasonable decomposition of the elastic shear constants of copper before proceeding with the analysis of the alloy data.

Several attempts have been made to calculate $C_R$, $C_R'$ directly by determining the pair potential $W_R$ by independent means. $C_F$, $C_F'$ can then be determined by subtraction. Calculations of $W_R$ have been made using pressure derivatives of the second-order elastic constants[22,33] and measured third-order and calculated fourth-order elastic constants.[34] Agreement is generally poor between the different calculations.

Other attempts have been made to calculate $C_F$, $C_F'$ directly. $C_R$, $C_R'$ can then be determined by subtraction. Sinha[10] has calculated the Fermi-energy contribution to the elastic shear constants using a local pseudopotential method. Collins[11] calculated the Fermi-energy contribution using a rigid-band model and measured Fermi-surface parameters. These calculations are summarized in Table VI along with the original Fuchs[9] calculation.

TABLE VI. Calculated lattice energy contributions to the elastic shear coefficients of copper in units of $10^{12}$ dyn cm$^{-2}$.

| $C = C_{44}$ | Fuchs[a] | Sinha[b] | Collins[c] |
|---|---|---|---|
| Electrostatic | 0.257 | 0.257 | 0.257 |
| Ion-core | 0.632 | 0.613 | 1.000 |
| Fermi | 0 | −0.038 | −0.425 |
| Total | 0.889 | 0.832 | 0.832 |
| $C' = \frac{1}{2}(C_{11} - C_{12})$ | | | |
| Electrostatic | 0.029 | 0.029 | 0.029 |
| Ion-core | 0.226 | 0.231 | 0.312 |
| Fermi | 0 | 0.006 | −0.075 |
| Total | 0.255 | 0.266 | 0.266 |

[a] Reference 9.
[b] Reference 10.
[c] Reference 11.

The Sinha and Collins calculations have been normalized to our extrapolated 0 °K elastic shear coefficients. The original Fuchs calculation is tabulated directly.

There is a large difference in the Fermi-energy contributions of Sinha and Collins. However, there are two characteristics that these results have in common. In each case, the Fermi contribution to $C$ is negative. Also, in each case, the magnitude of the Fermi contribution is greater for $C$ than for $C'$. This would be expected from the fact that the Fermi surface of copper contacts the $\{111\}$ faces of the Brillouin zone, and it is the motion of these faces that corresponds to the shear $C = C_{44}$. Both the Sinha and Collins calculations involve serious approximations, and it is difficult at this time to say which might be the most accurate. Hence, we will analyze the concentration dependence of the alloy elastic constants in terms of both of these decompositions.

If we include a Fermi-energy term, the changes in the elastic shear coefficients upon alloying are given by

$$\begin{aligned} \left(\frac{\partial C}{\partial x}\right)_a &= 2qC_E + \alpha C_R + aC_F , \\ \left(\frac{\partial C'}{\partial x}\right)_a &= 2qC_E' + \alpha C_R' + bC_F' . \end{aligned} \tag{9}$$

We have assumed a term linear in solute concentration for each Fermi-energy term because of the linearity of the measured elastic constants to 7 at.% Al. We have assumed different proportionality constants $a$ and $b$ for the Fermi terms because $C_F$ and $C_F'$ must depend differently on solute concentration.

For the $\alpha$–Cu-Al alloy system, $q$ should never be greater than 2. Therefore $aC_F$ and $bC_F'$ will make a positive contribution to the changes in the elastic shear coefficients. To estimate these, we

TABLE VII. Changes in the lattice energy contributions to the elastic shear coefficients for α–Cu-Al for solute concentrations < 7 at.% Al in units of $10^{10}$ dyn $\text{cm}^{-2}$/at. % Al.

| | $\left(\frac{\partial C}{\partial x}\right)_a$ | $2qC_E$ | $\alpha C_R$ | $aC_F$ | $\left(\frac{\partial C'}{\partial x}\right)_a$ | $2qC'_E$ | $\alpha C'_R$ | $bC'_F$ |
|---|---|---|---|---|---|---|---|---|
| Sinha[a] | | | | | | | | |
| $\alpha = -1$ | 0.89 | 1.03 | −0.61 | 0.47 | −0.03 | 0.12 | −0.23 | 0.08 |
| $\alpha = -2$ | 0.89 | 1.03 | −1.22 | 1.08 | −0.03 | 0.12 | −0.46 | 0.31 |
| Collins[b] | | | | | | | | |
| $\alpha = -1$ | 0.89 | 1.03 | −1.00 | 0.86 | −0.03 | 0.12 | −0.31 | 0.16 |
| $\alpha = -2$ | 0.89 | 1.03 | −2.00 | 1.86<br>2.3[c] | −0.03 | 0.12 | −0.62 | 0.47 |

[a] Reference 10.

[b] Reference 11.

[c] From Ref. 11, Fig. 5.

must assume values for the other parameters. Hence, we choose $q = 2$. To choose a value for $\alpha$, we refer to the work of Golding *et al.*[35] for Au-Ni alloys. Their analysis indicates that if we consider only Cu-Cu interactions and ignore Cu-Al and Al-Al interactions, then $\alpha = -2$. If the Cu-Al interaction is one-half the Cu-Cu interaction, and we ignore Al-Al interactions, then $\alpha = -1$. For the contributions to the copper elastic shear coefficients we take the results of Sinha[10] and Collins.[11] For each combination of these parameters, we can then calculate the Fermi contributions to the changes in the elastic shear coefficients. These are summarized in Table VII.

As noted previously, $aC_F$ and $bC'_F$ are always positive. In each case, $aC_F$ and $bC'_F$ correlate in an obvious way with $\alpha$ but differ only slightly for different decompositions of the copper shear coefficients. For example, although $C_F$ of Collins is more than 10 times the $C_F$ of Sinha, the respective $aC_F$ terms differ by less than a factor of 2.

## VI. DISCUSSION

The analysis of Sec. V indicates that there must be a Fermi-energy contribution $C_F$, $C'_F$ to the elastic shear coefficients of copper, and that the changes in these contributions $aC_F$, $bC'_F$ constitute a significant part of the changes in the elastic shear coefficients upon alloying. Previous calculations have indicated that, for copper, $C_F$ is negative and of greater magnitude than $C'_F$. The results here indicate that, upon alloying with aluminum, $aC_F$ is positive and of greater magnitude than $bC'_F$.

We have applied the same analysis to the changes in the elastic shear coefficients of the other noble metal alloy systems mentioned previously. We set $q$ equal to the excess valence of the solute, chose the elastic-constant decomposition of Collins, and set $\alpha$ equal to either $-1$ or $-2$. Then the same statement could be made in each case: $aC_F$ is positive and of greater magnitude than $bC'_F$.

The analysis to this point has been restricted to solute concentrations of less than 7 at.% Al. For larger solute concentrations, $C = C_{44}$ continues to increase linearly at the same rate while $C' = \frac{1}{2} \times (C_{11} - C_{12})$ decreases more sharply than before. In this composition range we can still assume that the electrostatic and ion-core repulsion contributions depend essentially in a linear fashion upon solute concentration for disordered alloys. However, it might be expected that the onset of SRO[27] would alter the electrostatic or ion-core repulsion contributions. This is essentially a question of geometry. Two models have been proposed for the configuration of Al ions in an ordered alloy, one with tetrahedral symmetry[26] and the other with octahedral symmetry.[27] In either case, if changes in the electrostatic or ion-core repulsion terms upon ordering were important, one would expect to see changes in the composition dependence of both $C$ and $C'$. However, we only observe a change in the composition dependence of $C'$ and, therefore, we doubt that changes in the electrostatic or ion-core repulsion terms predominate. Rather, we postulate that the gross features of the composition dependence of the elastic shear coefficients above 7 at.% Al can be explained in terms of the Fermi-energy contribution.

For a possible explanation of this hypothesis, we note the remarkable similarity between the changes in the elastic shear coefficients measured here and those calculated by Collins[11] using a rigid-band approximation. He calculated the Fermi-energy contributions to the elastic shear coefficients of copper, $C_F$ and $C'_F$, as a function of conduction-electron density $Z$. For all values of $Z$ large enough to cause intersection of the Fermi surface with the $\{111\}$ faces of the Brillouin zone, $C_F$ increased algebraically as a linear function of $Z$. This is in agreement with our observation of a linear increase in $C$ to the highest composition investigated. The slope of the calculated curve of

$C_F$ vs $Z$, our $aC_F$, was nearly independent of the choice of the copper band-gap parameters. Assuming that the aluminum solute atoms contribute three valence electrons to the copper conduction band ($q=2$), the result of the calculation is $aC_F = 2.3 \times 10^{10}$ dyn cm$^{-2}$/at.% Al. This value of $aC_F$ is included in Table VII. It is larger than the estimates based on our experimental results, but would be decreased if the effective $q$ was less than two for the $\alpha$–Cu-Al system. The calculated values of $C_F'$ are nearly independent of $Z$ for values of $Z$ near unity. At larger values of $Z$, the calculated $C_F'$ decreases rapidly. The same is true for our results for $C'$. However, referring to the quantitative analysis in Table VII, we see that we must require $\alpha \approx -1$ to obtain a negative $bC_F'$ for solute concentrations greater than 7 at.%. Although the magnitude and sign of the calculated $C_F'$ and $bC_F'$ near $Z=1$ depend upon the chosen band-gap parameters, the rapid decrease at larger $Z$ does not. This behavior is associated with the approach of the Fermi surface toward the $\{200\}$ faces of the Brillouin zone. It is important to note that, if this calculation is valid, the composition dependence of $C$ and $C'$ would be explained without invoking changes due to SRO.

This interpretation of the composition dependence of the shear coefficients of the $\alpha$-Cu-Al alloy system indicates an increase in conduction-electron density with increasing Al concentration. This is in agreement with other experiments on this alloy system. The electronic specific heat,[31,32] which increases upon the addition of aluminum to copper, can be interpreted in terms of a rigid-band model corrected for the change in the electron-phonon enhancement of the electronic density of states upon alloying.[36] Also, observation of positron annihilation spectra[37] for compositions to 10 at.% Al indicate that the Fermi-surface neck diameter is increasing. Each of these experiments indicates an increase in conduction-electron density consistent with a simple scaling of the copper Fermi surface.

In addition, measurements by Scattergood *et al.*[27] of diffuse x-ray scattering from specimens with 11 and 16 at.% Al indicate that the Fermi surface is expanding in the ⟨110⟩ directions. These measurements depend upon the presence of order in the alloy crystals. In fact, Scattergood *et al.* propose that the composition dependence of the SRO can be analyzed in terms of the Fermi-energy contribution to the effective interatomic potential. This is in accord with our basic suggestion that it is the Fermi-energy contribution that determines the gross features of the dependence of the elastic shear coefficients on alloy compsoition.

It would be surprising if a rigid-band model of the $\alpha$–Cu-Al band structure contained sufficient physical content to explain, even qualitatively, the composition dependence of the elastic shear coefficients, especially in the range above 7 at.% Al. However, the similarity between experiment and the calculation described above is striking and warrants presentation. One cautionary note should be interjected. Recent measurements of the interband optical absorption for the $\alpha$-Cu-Al alloy system[38,39] may indicate that the conduction band both fills and sinks in such a way that the separation between the Fermi level and the top of the $d$ bands remains constant. This would indicate changes in the alloy band structure in addition to changes in the conduction-electron density. It is also observed that the character of the interband optical absorption changes for concentrations above 7 at.% Al. This might indicate that the onset of SRO has some influence on the band structure. However, there is no way, at present, to include these effects in a calculation of the composition dependence of the elastic shear coefficients. This must remain the object of further study.

## VII. CONCLUSIONS

The elastic constants and their temperature derivatives have been measured near room temperature for single-crystal $\alpha$–Cu-Al alloys for compositions to 13 at.% Al. The important experimental results can be summarized as follows: The elastic shear coefficient $C = C_{44}$ increases linearly over the entire composition range investigated. The elastic shear coefficient $C' = \frac{1}{2}(C_{11} - C_{12})$ decreases linearly with increasing solute concentration to approximately 7 at.% Al. For higher Al concentration, $C'$ decreases at a greater rate. The bulk modulus determined from the measured elastic constants $[B = (\frac{1}{3})\,(C_{11} + 2C_{12})]$ decreases in a linear manner with increasing Al concentration. However, when the observed change is corrected for lattice expansion, it is found that $B$ would increase upon alloying at constant volume. The temperature derivatives of the elastic constants depend only weakly on alloy composition. The largest systematic change occurs for $(\partial C'/\partial T)$.

The changes in the elastic constants of the alloys extrapolated to 0 °K using the measured temperature derivatives have been used to calculate the change in the Debye temperature $\Theta_0$ with increasing Al concentration. For solute concentrations less than 7 at.% Al, we find that $\Theta_0$ increases at a rate given by $(d\Theta_0/dx) = 0.69$ °K/at.% Al. For solute concentrations greater than 7 at.% Al, $\Theta_0$ increases at a lesser rate. The increase in $\Theta_0$ is in agreement with that determined from specific-heat measurements.

The changes in the elastic shear coefficients upon alloying, corrected for the effects of lattice expansion and extrapolated to 0 °K, have been analyzed in terms of a generalized Fuchs theory of homogeneous deformation. We have concluded that a conduction-electron energy term must be included in calculating the shear coefficients of copper and that changes in this conduction-electron term with increasing Al concentration make a significant contribution to the changes in the elastic shear coefficients upon alloying. We also conclude that it is the conduction-electron term that is responsible for the gross features of the composition dependence of the shear coefficients above 7 at.% Al. These results indicate an increase in conduction-electron density with increasing Al concentration. This is in agreement with other experiments on the α–Cu-Al alloy system.

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