[5] P. H. Carr and S. Foner, J. Appl. Phys. 31, S5344 (1960).

[6] J. Wucher, J. Rech. Cent. Nat. Rech. Sci. Lab. Bellevue (Paris) 21, 254 (1952); M. Foëx and J. Wucher, Compt. Rend. 241, 184 (1955).

[7] A. J. MacMillan, Laboratory for Insulation Research, Massachusetts Institute of Technology, Technical Report No. 172, 1962 (unpublished).

[8] D. J. Arnold and R. W. Mires, J. Chem. Phys. 48, 5 (1968).

[9] R. Jesser and D. Silhouette, Compt. Rend. 2648, 1123 (1967).

[10] A. Menth and J. P. Remeika, Phys. Rev. B 2, 3756 (1970).

[11] E. D. Jones, Phys. Rev. 137, A978 (1965).

[12] K. Kosuge, J. Phys. Chem. Solids 28, 1613 (1967).

[13] R. M. Moon, J. Appl. Phys. 41, 883 (1970); Phys. Rev. Letters 25, 527 (1970).

[14] E. P. Warekois, J. Appl. Phys. 31, S346 (1960).

[15] E. D. Jones, J. Phys. Soc. Japan 27, 1962 (1969).

[16] M. Foex, J. Goldstaub, R. Jeffrey, R. Lyand, R. Wey, and J. Wache, J. Rech. Cent. Nat. Rech. Sci. Lab. Bellevue (Paris) 21, 237 (1952).

[17] D. B. McWhan, T. M. Rice, and J. P. Remeika, Phys. Rev. Letters 22, 887 (1969).

[18] A. C. Gossard, D. B. McWhan, and J. P. Remeika, Phys. Rev. B 2, 3762 (1970).

[19] A. Jayaraman, D. B. McWhan, J. P. Remeika, and P. D. Dernier, Phys. Rev. B 2, 3751 (1970).

[20] K. Kosuge and S. Kachi, J. Phys. Soc. Japan 20, 627 (1965).

[21] D. B. McWhan, A. Menth, and J. P. Remeika, Proceedings of the International Conference on Magnetism, Grenoble, 1970 (unpublished).

[22] A. Menth, A. C. Gossard, and J. P. Remeika, Proceedings of the International Conference on Magnetism, Grenoble, 1970 (unpublished).

[23] W. W. Warren, Jr., A. C. Gossard, and M. D. Banus, J. Appl. Phys. 41, 881 (1970).

[24] M. D. Banus and T. B. Reed, in *The Chemistry of Extended Defects in Non-Metallic Solids*, edited by L. Eyring and M. O'Keefe (North-Holland, Amsterdam, 1970), p. 488.

[25] J. Umeda, S. Ashida, H. Kusumoto, and K. Narita, J. Phys. Soc. Japan 21, 1461 (1966).

[26] Koji Kosuge, J. Phys. Soc. Japan 22, 551 (1967).

[27] T. M. Rice, D. B. McWhan, and W. F. Brinkman, *Proceedings of Tenth International Conference on the Physics of Semiconductors*, edited by S. P. Keller, J. C. Hensel, and F. Stern (U. S. Atomic Energy Commission Division of Technical Information, Oak Ridge 1970), p. 293.

[28] Koji Kosuge, J. Phys. Chem. Solids 28, 1613 (1967).

[29] W. W. Warren, Jr. (unpublished).

[30] Mark Rubinstein, Phys. Rev. B 2, 4731 (1970).

[31] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters 9, 262 (1962).

[32] G. M. Zverev and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. 38, 449 (1960) [Soviet Phys. JETP 11, 330 (1960)].

[33] John B. Goodenough, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors*, edited by S. P. Keller, J. C. Hensel, and F. Stern (U. S. Atomic Energy Commission Division of Technical Information, Oak Ridge, 1970), p. 304.

[34] V. Heine and L. F. Mattheiss (unpublished).

[35] Y. Yafet and V. Jaccarino, Phys. Rev. 133, A1630 (1964).

[36] T. Moriya, Progr. Theoret. Phys. (Kyoto) 16, 23 (1956).

[37] V. Jaccarino, *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. IIA, p. 333.

[38] W. D. Knight, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 2, p. 93.

[39] J. Owen and D. R. Taylor, J. Appl. Phys. 39, 791 (1968).

PHYSICAL REVIEW B VOLUME 3, NUMBER 12 15 JUNE 1971

Elastic Constants of Copper-Rich Alloys with Gold†

S. G. O'Hara and B. J. Marshall
Department of Physics, Texas Tech University, Lubbock, Texas 79409

(Received 30 October 1970)

The elastic constants of Cu-(0.23 at.%)Au, Cu-(2.8 at.%)Au, and Cu-(10.0 at.%)Au have been experimentally measured over the temperature range 300–4.2 °K. The elastic constants at 0 °K have been fitted with the Neighbors-Smith model for shear elastic constants of dilute monovalent-metal alloys.

INTRODUCTION

Cohesion in a metal crystal is especially complicated by the influence of the electron sea. As a result, the elastic constants of metal single crystals are difficult to relate to atomic theory, except for a few special cases. Fuchs,[1] for instance, has proposed a theory of elastic constants for monovalent metals which gives rather good agreement with experimental data for the alkali metals and the noble metals.[2,3] This model deals with shear strains, which do not affect the atomic volume of the Wigner-Seitz cell surrounding each metal ion. As a result the shear elastic constants $c' = \frac{1}{2}(c_{11} - c_{12})$ and c_{44}

TABLE I. Lattice spacings in angstroms and densities ρ in g/cm^3 for Cu-(0.23 at.%)Au, Cu-(2.8 at.%)Au, and Cu-(10.0 at.%)Au at 300 °K.

Alloy	Lattice spacing	Density
Cu-(0.23 at.%)Au	3.616	8.970
Cu-(2.8 at.%)Au	3.632	9.326
Cu-(10.0 at.%)Au	3.669	10.340

depend primarily on two factors: the change in the potential energy of the electrons due to distortion of the edges of the Wigner-Seitz cell, and exchange repulsion due to overlap of closed shells of two neighboring ions.

In the case of alloys one encounters even greater difficulty in explaining the results of experimental determinations of the elastic constants. Existing theories tend to be modifications of a pure-metal theory such as that of Fuchs. In particular, Neighbors and Smith have proposed a semiempirical theory for alloys composed of slightly diluted monovalent metals.[4] According to this model, the elastic constants of such an alloy are determined from the elastic constants of the host and the concentration of the impurity ions.

In this study we have measured the adiabatic elastic constants, over the temperature range 300–4.2 °K, of copper plus 0.23, 2.8, and 10 at.% gold. It would be expected that a dilute alloy of a noble metal with a noble metal would provide an optimum test of alloy models derived from the monovalent-metal model. Copper and gold are completely miscible in the alloy state, so that a study of these alloys should characterize the properties of gold dissolved in copper over a fair range of compositions. Furthermore, the use of such dilute alloys excludes the complications caused by superlattices in higher concentrations of the alloy family.[5]

EXPERIMENTAL

The single crystals were obtained from Materials Research Corporation in the forms of circular cylinders approximately 5 in. in length by 0.625 in. in diameter. The [100] and [110] specimens were then cut from the center of each cylinder with an Elox model TQH-31 electric discharge machine, oriented by standard Laue x-ray back reflection, and then the end faces were polished parallel by the electric discharge machine. Lengths of the [100] and [110] specimens were approximately 2.5 and 1.2 cm, respectively, at room temperature. The end faces were parallel to within 0.0005 cm and the crystalline directions were within 1.0° of being perpendicular to the end faces.

The concentration of gold in each alloy crystal

TABLE II. Elastic constants c_{11}, c_{44}, c', and c_{12} in units of 10^{11} dyn/cm^2, densities in units of g/cm^3, bulk moduli in units of 10^{11} dyn/cm^2, and anisotropy unitless.

T	c_{11}	c_{44}	c'	c_{12}	B	A	ρ
Cu-(0.23 at.%)Au							
0	17.825	8.206	2.602	12.621	14.355	3.154	9.060
10	17.825	8.206	2.602	12.621	14.355	3.154	9.060
20	17.821	8.202	2.602	12.617	14.351	3.152	9.060
30	17.816	8.196	2.601	12.614	14.347	3.151	9.060
80	17.748	8.113	2.584	12.580	14.302	3.140	9.054
200	17.372	7.799	2.464	12.444	14.086	3.165	9.013
300	17.000	7.419	2.340	12.320	13.879	3.171	8.970
Cu-(2.8 at.%)Au							
0	17.775	7.930	2.498	12.779	14.445	3.175	9.420
10	17.775	7.929	2.498	12.779	14.445	3.174	9.420
20	17.762	7.922	2.497	12.768	14.432	3.173	9.420
30	17.749	7.911	2.495	12.759	14.422	3.171	9.420
80	17.649	7.843	2.473	12.703	14.351	3.171	9.414
200	17.281	7.632	2.369	12.543	14.122	3.222	9.371
300	16.917	7.392	2.265	12.387	13.897	3.264	9.326
Cu-(10.0 at.%)Au							
0	18.347	7.850	2.450	13.447	15.081	3.204	10.44
10	18.347	7.850	2.450	13.447	15.081	3.204	10.44
20	18.345	7.849	2.448	13.449	15.081	3.206	10.44
30	18.337	7.846	2.445	13.447	15.076	3.209	10.44
80	18.226	7.793	2.417	13.392	15.004	3.224	10.43
200	17.833	7.553	2.292	13.249	14.778	3.295	10.39
300	17.467	7.313	2.186	13.095	14.552	3.345	10.34

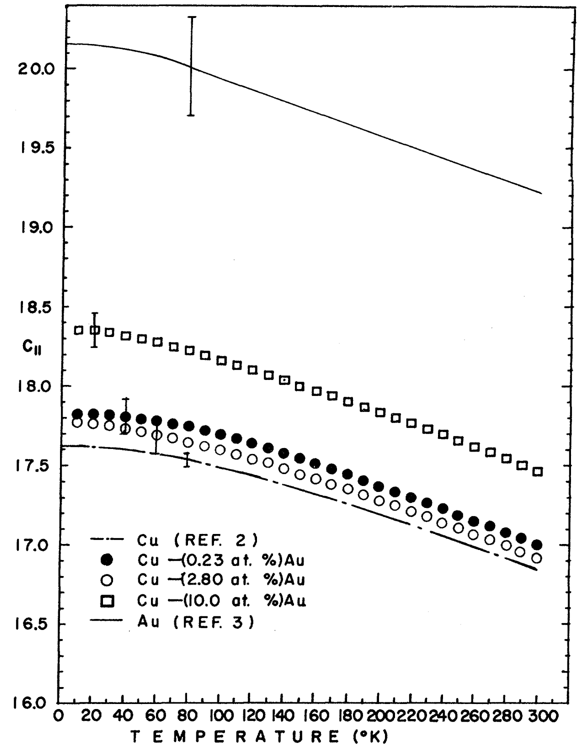

FIG. 1. Elastic constant c_{11} of Cu, Cu-(0.23 at.%)Au, Cu-(2.8 at.%)Au, Cu-(10.0 at.%) Au, and Au in units of 10^{11} dyn/cm^2.

was also determined in this laboratory. The analyses were made on a Jarrell-Ash atomic absorption unit with reference standards prepared from spectroscopically pure copper and gold.

Since gold atoms are larger than the copper host atoms, it seemed probable that alloying would change the lattice spacing of the pure copper. Therefore, we have made a determination of the lattice spacings of the three alloys. Powder filings of each alloy were annealed at 600 °C for two weeks and then analyzed on an x-ray diffractometer. It was found that the lattice spacings for Cu-(0.23 at.%) Au and Cu-(2.8 at.%) Au agreed very well with Vegard's law.[6] For Cu-(10.0 at.%) Au the results were inconclusive due to weakness and broadening of the diffraction peaks. Thus, we have used Vegard's law and the results of the chemical analysis to determine the lattice spacing for the 10% concentration. The density of each of the alloys was calculated from its concentration of gold, its lattice spacing, and the density of pure copper. The density of pure copper, $\rho = 8.933$ gm/cm^3, was calculated from its lattice spacing of 3.615 Å given in the American Society for Testing and Materials (ASTM) card file. Table I gives the values of the concentrations and corresponding lattice spacings and densities at $T = 300$ °K.

Since these alloys have the symmetry of a cubic crystal there are only three independent elastic constants, c_{11}, c_{44}, and c_{12}.[7] To obtain c_{11} and c_{44} one simply measures the velocities (V) of 10-MHz longitudinal and transverse sound waves propagated in the [100] direction. Then if the density ρ is known, the following relations may be used: $c_{11} = \rho V_L^2$ and $c_{44} = \rho V_T^2$. To obtain c_{12}, one measures the velocity (V_T') of a transverse wave propagated along the [110] direction with its particle motion polarized perpendicular to the [001] direction, giving $c' = \rho V_T'^2 = \frac{1}{2}(c_{11} - c_{12})$.

The method employed to measure the sound velocities in the crystals was the well-known pulse-echo technique. The equipment has been described in an earlier publication.[8] At least six echoes were used for each measurement.

The bond between the crystal and transducer was Nonaq stopcock grease for the temperature range 100–300 °K. In the temperature range 4.2–200 °K Dow Corning DC-11 was used. Data were taken in such a manner that the results obtained when using the two different binders overlapped by at least a

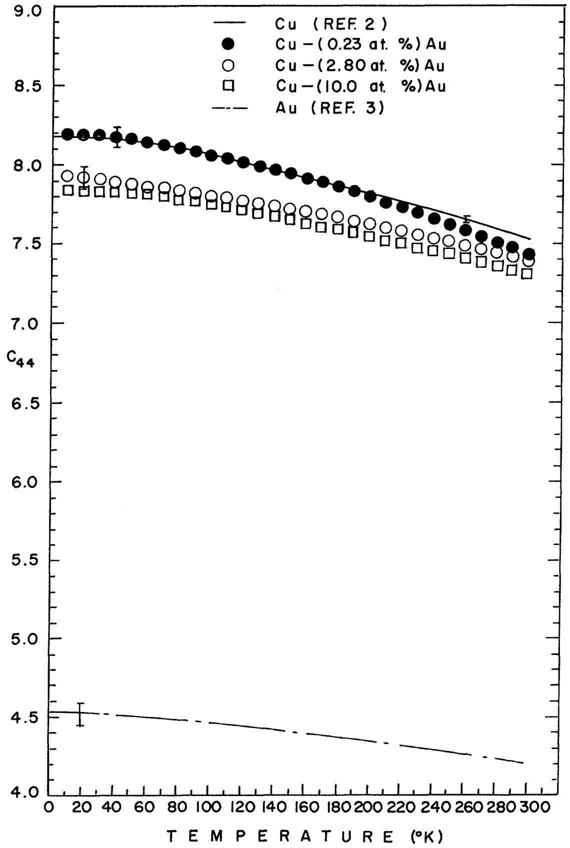

FIG. 2. Elastic constant c_{44} of Cu, Cu-(0.23 at.%)Au, Cu-(2.8 at.%)Au, Cu-(10.0 at.%)Au, and Au in units of 10^{11} dyn/cm^2.

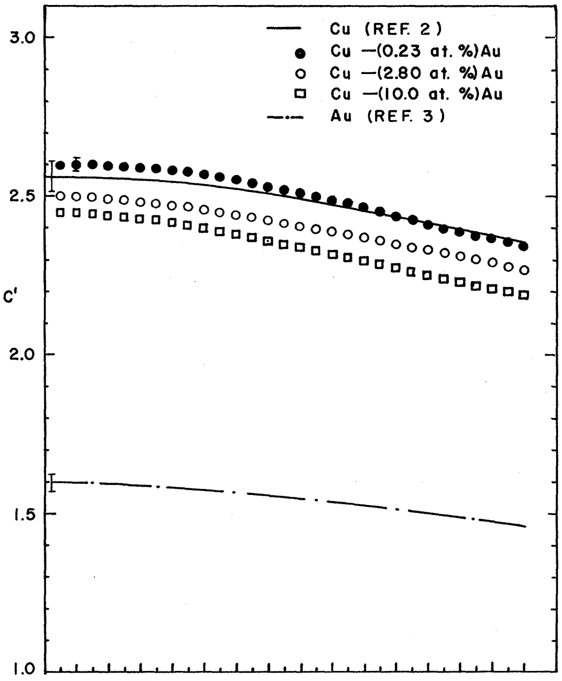

FIG. 3. Elastic constant c' of Cu, Cu-(0.23 at.%)Au, Cu-(2.8 at.%)Au, Cu-(10.0 at.%)Au, and Au in units of 10^{11} dyn/cm^2.

temperature range of 40 °K. The data always agreed in the region of overlap.

In the temperature range 80–300 °K, the crystal temperature measurements were made with a copper-constantan thermocouple. Temperatures in the range 4.2–80 °K were measured with a Cryo-Cal germanium resistance thermometer. The emf measurements were taken with a Leeds and Northrup six-dial potentiometer facility.

RESULTS

In order to calculate the elastic constants of these alloys as a function of temperature, it is necessary to know the temperature dependence of their lengths and densities. There are no data available on the temperature dependence of these properties. Therefore, we have utilized the linear expansion coefficient of pure copper for these calculations. This is a reasonable assumption since the alloy differs in composition only slightly from pure copper. Furthermore, this total correction in length constitutes a very small correction in the elastic constants.

The linear expansion coefficient of copper $\alpha(T)$ has been measured by Fraser and Hallett from 20 to 90 °K,[9] and by Leksima and Novikova from 90 to 1323 °K.[10]

To account for the thickness of the binder, a correction was made in the measured echo round-trip times. A correction of 0.04 μsec was subtracted from times for transverse waves, and a correction of 0.03 μsec was subtracted from these times for longitudinal waves.[11]

TABLE III. Elastic constants c_{11}, c_{44}, and c_{12} (0 °K) in units of 10^{11} dyn/cm^2 and Debye temperature Θ in Kelvin degrees.

Element or alloy	c_{11}	c_{44}	c_{12}	Debye Θ
Cu	17.620	8.177	12.494	345.4
Cu-(0.23 at.%)Au	17.825	8.206	12.621	329.7
Cu-(2.8 at.%)Au	17.775	7.930	12.779	319.4
Cu-(10.0 at.%)Au	18.347	7.850	13.447	310.9
Cu_3Au	18.490	6.870	13.530	283.8
Au	20.163	4.544	16.967	162.6

The results of the calculations of the elastic constants are given in Table II. Also included in Table II are the densities and bulk moduli calculated from the equation $B=\frac{1}{3}(c_{11}+2c_{12})$. Estimated maximum possible errors in the values of these parameters are c_{11}, ± 0.6%; c_{44}, ± 0.8%; c', ± 0.8%; and c_{12}, ± 0.9%. Figures 1–3 show the temperature dependence of the elastic constants.

The Debye temperatures have been calculated in accordance with the method of Betts, Bhatia, and Wyman.[12] Table III provides a comparison at 0 °K of the elastic constants and Debye temperatures of pure copper,[2] Cu-(0.23 at.%)Au, Cu-(2.8 at.%)Au, Cu-(10.0 at.%)Au, Cu_3Au,[13] and pure gold.[3]

The anisotropy of each crystal has been calculated by the equation[14] $A=c_{44}/c'$ and is also included in Table II.

DISCUSSION

We have fit our data to a model for dilute alloys of monovalent metals proposed by Neighbors and Smith.[4] Based on Fuch's[1] model for monovalent metals they have proposed that the changes in the shear constants of a monovalent metal upon alloying are given by

$$\Delta c = c_E(Z^2-1)+c_I\alpha x\ ,\qquad \Delta c' = c'_E(Z^2-1)+c'_I\alpha x\ . \tag{1}$$

The constants c_E, c_I, c'_E, and c'_I are obtained from the experimentally measured elastic constants

TABLE IV. Values of α and Z using two different methods of lattice-parameter correction.

	First method		Second method	
Alloy	α	Z	α	Z
Cu-(0.23 at.%)Au	0.120	0.98	0.014	1.00
Cu-(2.8 at.%)Au	0.024	0.98	0.022	1.08
Cu-(10.0 at.%)Au	0.029	1.03	0.024	1.28

of the host monovalent metal combined with calculations in accordance with Fuch's model. The parameter Z has been interpreted to be the average electron to atom ratio in the alloy. The parameter α is related to the strength of closed electron shell interactions between added solute ions and the host monovalent ions. For dilute alloys, α should be a constant for a given alloy family. The atomic concentration of the dilute constituent of the alloy is denoted by x.

Equations (1) are intended to represent the changes in the elastic constants due to the effects of alloying only. Therefore, before the values of Z and α can be determined, it is necessary to correct Δc, $\Delta c'$, c_E, c_I, c_E', and c_I' for the changes in the lattice parameter of the monovalent metal which occur upon alloying. Using the method of correction given by Neighbors and Smith,[4] we have obtained values of Z and α given in Table IV under the heading "First method." We have also used the pressure derivatives of the elastic constants of copper[15] to obtain these lattice-parameter corrections. Values of Z and α obtained by this method are also listed in Table IV under the heading "Second method." Values of the shear elastic constants for copper used in both methods of calculation were values extrapolated to 0 °K from the work of Overton and Gaffney.[2] All values used for the shear elastic constants of the alloys were also extrapolated 0 °K values.

Since Z is a measure of the average electron to atom ratio in an alloy, it should have the numerical value of 1.00 for the Cu-Au family. An examination of the data in Table IV would indicate that the first lattice-parameter-correction method gives for α and Z a more acceptable and consistent value for the three alloys than does the second method.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Charles S. Smith, Jr., and Dr. W. O. Milligan for their helpful suggestions and discussions. We are also deeply appreciative to Dr. J. R. Craig and Dr. W. D. Miller of our geology department for their excellent assistance.

---

†Work supported by the Robert A. Welch Foundation of Texas.

[1] K. Fuchs, Proc. Roy. Soc. (London) A153, 622 (1938).

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

[3] J. R. Neighbors and G. A. Alers, Phys. Rev. 111, 707 (1958).

[4] J. R. Neighbors and C. S. Smith, Acta Met. 2, 591 (1954).

[5] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1953), pp. 198–203.

[6] W. B. Pierson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, New York, 1958), pp. 411, 412, 601.

[7] H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7, pp. 214-349.

[8] B. J. Marshall, D. O. Pederson, and G. G. Dorris, J. Phys. Chem. Solids 28, 1061 (1967).

[9] D. B. Fraser and A. C. Hallett, Can. J. Phys. 43, 195 (1965).

[10] I. E. Leksima and S. I. Novikova, Fiz. Tverd. Tela 5, 1094 (1963) [Soviet Phys. Solid State 5, 798 (1963)].

[11] L. J. Slutsky and C. W. Garland, Phys. Rev. 107, 972 (1957).

[12] D. D. Betts, A. B. Bhatia, and M. Wyman, Phys. Rev. 104, 37 (1956).

[13] P. A. Flinn, G. M. McManus, and J. A. Rayne, J. Phys. Chem. Solids 15, 189 (1960).

[14] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1966), p. 118.

[15] W. B. Daniels and C. S. Smith, Phys. Rev. 111, 713 (1958).