Pressure Derivatives of the Elastic Constants of Copper, Silver, and Gold to 10,000 Bars

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The pressure derivatives of the elastic constants of the homologous series of metals, copper, silver, and gold have been measured over the pressure range from 0 to 10 000 bars, using a modified ultrasonic pulse-echo method. Means have been devised to measure the *change* of elastic constant with pressure as directly as possible. The values found for the pressure derivatives of the elastic constants are as follows:

	Cu	Ag	Au
dB_s/dP	5.59	6.18	6.43
dC/dP	2.35	2.31	1.79
dC'/dP	0.580	0.639	0.438

The notation $C=C_{44}$, $C'=(C_{11}-C_{12})/2$, and $B_s=(C_{11}+2C_{12})_s/3$ has been used. The data for each metal, of the three elastic constants and their pressure derivatives, have been interpreted in terms of conventional theory. The theoretical contributions of long-range interactions have been subtracted off and the remainder attributed to short-range nearest-neighbor interaction. The analysis indicates that these must be non-central, many-body interactions in order to account for the shear constants and especially their pressure derivatives. The many-body character of the interactions is of rapidly increasing importance in the sequence copper, silver, and gold.

INTRODUCTION

It is well known that in the theory of the cohesion of copper it is necessary to introduce a short-range repulsive interaction between ion cores in order to account for the observed value of the compressibility. This interaction is generally represented empirically by a two-parameter exponential potential which is a function of ion separation only. It is an important interaction in theories of the mechanism of diffusion in this metal and several workers have followed the procedure of evaluating the parameters by means of the observed values of the single crystal elastic stiffnesses.[1–3] This procedure is quite satisfactory for the purpose, but the converse procedure of attempting to account in detail for the elastic stiffnesses in terms of a two-parameter exponential repulsion is less satisfactory. This failure is seldom pointed out explicitly; it becomes more and more apparent, however, when one examines the single-crystal elastic stiffnesses of the similar metals, silver and gold.

The contribution of a short-range interaction becomes more and more important relative to long-range interactions as one successively examines the binding energy, the equilibrium condition, and the elastic stiffnesses. Going one step further, the pressure derivatives of the elastic stiffnesses will be determined almost entirely by the short-range interactions, and it is with a view to studying such interactions under these favorable circumstances that the present work was undertaken. It was felt that it would be desirable to study the entire homologous series, copper, silver, and gold, since the interpretation for these metals is expected to be qualitatively similar.

[1] H. B. Huntington and F. Seitz, Phys. Rev. 61, 315 (1942).
[2] H. B. Huntington, Phys. Rev. 91, 1092 (1953).
[3] C. Zener, Acta Cryst. 3, 346 (1950).

The pressure derivative of the bulk modulus is a primary result in the classic work of Bridgman[4]; the dependence on pressure of the shear modulus of a few polycrystalline materials has been studied by Birch.[5] The only previous study of the pressure dependence of the elastic constants of single crystals is that of Lazarus,[6] who, in a pioneering paper, reported on KCl, NaCl, CuZn, Cu, and Al. The present work follows Lazarus in using the ultrasonic pulse-echo technique of elastic constant determination. This technique is ideal for observations in the ambient of a liquid under high pressure since it is a nonresonant method. Our observational procedure has, however, been different from that of Lazarus. The high-pressure apparatus has been constructed and the measuring equipment has been modified in such a way that the method is essentially a differential one, in which the *change* in elastic stiffness is observed directly.

EXPERIMENT

High-Pressure System

The high-pressure system consisted of an hydraulic pump operating on a 7.4:1 piston intensifier. The apparatus is based on a system used by Jacobs[7] for optical absorption studies.[8] Following a suggestion by Dr. D. P. Johnson of the National Bureau of Standards, Octoil-*S* was used as the high-pressure fluid. The superior lubricating properties of this oil as well as its low-pressure coefficient of viscosity make it an ideal

[4] P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, London, 1952), Chap. VI.
[5] F. Birch, J. Appl. Phys. 8, 129 (1937).
[6] D. Lazarus, Phys. Rev. 76, 545 (1949).
[7] I. S. Jacobs, Phys. Rev. 93, 993 (1953).
[8] We wish to thank Professor A. W. Lawson of the University of Chicago for the blue prints of Jacobs' apparatus and for many valuable suggestions.

fluid in the range covered by this work. Pressure was measured using the resistance of a manganin wire coil as discussed by Bridgman,[4] and by Darling and Newhall.[9] The freezing pressure of mercury at 0°C, 7640 kg/cm², was used as the high-pressure calibration point. Electrical leads into the bomb for the pressure gauge and for the experimental plug were insulated by pipestone cones.[10]

The design adopted for sealing the closure plugs and the moving intensifier piston are described in a recent article.[11] It will suffice to say here that these were such that it was possible to cycle the pressure repeatedly from 0 to 10 000 bars, permitting the acoustic measurements to be made in a particularly simple way, described in the section on measurements.

Sample Preparation

The copper single crystals and the silver crystal were grown in this laboratory using a modified Bridgman method. The gold crystal was purchased from the Virginia Institute for Scientific Research. The copper and silver specimens were prepared by first cutting off the crystals to the desired orientation and length (from 1 to 3 cm) using a water-cooled abrasive cutoff wheel. The gold crystal was received at the desired orientation and length. After etching to remove any cold-worked layer, the specimens were waxed into a lapping block and lapped flat using metallographic papers ranging from No. 2 to No. 3/0 grade. After this, each acoustic surface was given another light etch and the samples were lapped with Buehler 1557 AB levigated alumina in oil on a flat glass plate. A final very light etch completed the treatment. This final etch gave the surface a slight "tooth" which aided the cement in holding the transducer to the surface. It was possible after this treatment to obtain reasonably sharp Laue back reflection spots directly from the acoustic surfaces.

Grade 629 Polyethylene by Semet-Solvay Division, Allied Chemical and Dye Corporation was found quite satisfactory for cementing the 10 mc X- and Y-cut quartz transducers to the specimen. Every attempt was made to obtain reproducibility in attaching the transducers from run to run. The polyethylene was melted on the heated specimen, and the transducer placed on it with the desired orientation relative to the crystallographic axes of the specimen. The assembly was allowed to cool, then an 800 g weight was placed on top of it, and the assembly was again heated to well above the melting temperature of the polyethylene for several hours and allowed to cool slowly. The rf electrode was painted directly onto the transducer with du Pont 4817 silver paint. As was observed by Lazarus,[6] the quartz transducer shattered each time a set of pressure runs was made. The preponderance of cracks running perpendicular to the axis of greatest compressibility of the quartz in the case of the Y-cut transducers seems to indicate that it is differential compressibility between quartz and sample which causes the cracking. The cracking did not prevent taking of data, but pulse-echo amplitude usually decreased during a data run. If the metal crystal was etched after measurements had been made at high pressure, the lines along which the quartz had cracked would show up. Accompanying this effect was a slight broadening of the Laue back reflection spots. The fact that no significant dependence of the measured pressure derivatives on specimen length was found in this work indicates that this slight cold-working of the surface is relatively unimportant.

Measurements

For each crystal, the longitudinal and two transverse wave velocities, and their *changes* with pressure, were measured using the ultrasonic pulse-echo method[12–14] with modifications.[15] The gear used for this work incorporated a Tektronix type 121 wide band preamplifier and displayed the unrectified echo pattern on the face of the detecting oscilloscope. Thus the details of each pulse echo were shown, the 10-Mc/sec structure of each echo being observed along the time axis. The sweep delay helipot of the Dumont 256 D A/R oscilloscope was removed and combined with external resistance boxes in such a way as to make measurement of 0.001-μsec *changes* of echo arrival time possible. In practice the method used to take data on the changes of transit time with pressure was to measure the *change* in time of arrival of a particular maximum of the 10-Mc/sec echo structure, relative to a fixed time marker, as the pressure was cycled up and then down several times. It is felt that this arrangement using unrectified pul-

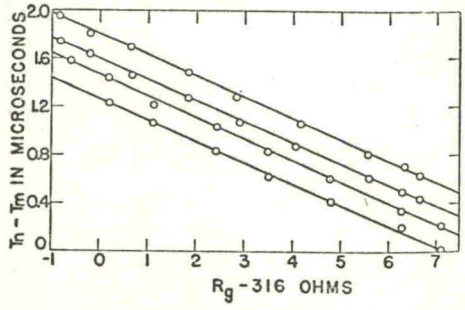

FIG. 1. Typical data plot showing difference between time of arrival of one maximum of an echo, and a nearby time marker, as a function of pressure gauge coil resistance. The curves representing different runs are displaced for the sake of clarity. The data apply to runs 1 through 4 of experiment No. 1 for C_{44} waves in the 1.86 cm long copper crystal. The pressure range covered is about 9800 bars.

[9] H. E. Darling and D. H. Newhall, Trans. Am. Soc. Mech. Engrs. 75, 311 (1953).
[10] P. W. Bridgman, Proc. Am. Acad. 74, 11 (1940).
[11] W. B. Daniels and A. A. Hruschka, Rev. Sci. Instr. 28, 1058 (1957).
[12] H. B. Huntington, Phys. Rev. 72, 321 (1947).
[13] J. R. Neighbours and C. S. Smith, J. Appl. Phys. 21, 1[illegible] (1950).
[14] Neighbours, Bratten, and Smith, J. Appl. Phys. 23, [illegible] (1952).
[15] S. Eros and J. R. Reitz, J. Appl. Phys. 29, 683 (1958).

...oes is less prone to errors arising from change of ...se-echo shape with pressure than is that using gear ...ich displays the rectified pulse-echoes. A typical ...ata plot is given in Fig. 1 showing the difference be...een time of arrival of one of the maxima of echo No. 7 ... the C_{44} wave in a 1.9-cm long copper crystal and a ...ed time-marker, as a function of pressure gauge coil ...istance. The pressure range indicated is about 9800 ...rs. Data points were taken about 5 min after each ...ssure change in order that the system be near ...ermal equilibrium. Absence of hysteresis justifies the ...e interval chosen. Strictly speaking one is interested ...ly in the initial slopes of these curves, but experi...entally all the plots are linear over the pressure range ...ed. The slope of this line can be determined by a ...ast squares method and this slope, together with the ...easured zero pressure transit time, enables one to ...mpute the quantity $(nT_0)^{-1}dT_n/dR_g$, where T_0 is the ...ro pressure transit time, n is the number of the echo ...der observation, T_n is the observed time of arrival ... the nth echo and R_g is the pressure gauge coil re...tance. Since one can express the pressure gauge coil ...ibration as $dP=KdR_g$, and $T_n(P)=nT(P)$, the ...antity $k^{-1}(nT_0)^{-1}dT_n/dR_g$ represents the fractional ...ange of transit time with pressure, $(T_0)^{-1}dT/dP$.

A sequence of observations made with increasing ...ssure or with decreasing pressure will be called a run. ...ts of runs made with a given transducer cemented in ...ce will be called an experiment. Each value of $\Gamma)^{-1}dT/dP$ which has been used is the result of at ...st two experiments each of which consisted of at ...st two runs. In the case of copper this procedure was ...llowed for each of three crystals.

For crystals of nearly [110] orientation the equations ...ating transit times to elastic constants are given by

$$\begin{aligned} Y_2&=B_s+4(\tfrac{1}{3}-\Gamma)C'+4\Gamma C,\\ Y_4&=C+2a_1(C'-C),\\ Y_5&=C+2a_2(C'-C), \end{aligned} \tag{1}$$

...here

$$Y_2=\rho V_2^2=4\rho L^2/T_2^2,\quad Y_4=\rho V_4^2=4\rho L^2/T_4^2,\quad Y_5=\rho V_5^2=4\rho L^2/T_5^2, \tag{2}$$

T_2 is the transit time for the longitudinal wave, and T_4 ...d T_5 refer to the slow and fast shear wave transit ...mes, respectively. L is the length of the specimen ...etween acoustic faces and ρ is the density of the ...terial under study. The notation, $C=C_{44}$, C' ...$(C_{11}-C_{12})/2$ and $B_s=(C_{11}+2C_{12})/3$, has been used. ... denotes the adiabatic bulk modulus. The quantities ..., a_1 and a_2 are orientation functions[14] which are ...lependent of pressure for cubic materials. For ori...tations near [110], a_1 is about 0.5 and a_2 is nearly ...ro. For exactly [110] orientation one could write: ...$=C'$, $Y_5=C$. That is, C' is determined by Y_4 only, ...d C is found from Y_5 only. Taking the derivative ...th respect to pressure, of each equation relating the Y's and the elastic constants, one obtains

$$\begin{aligned} \frac{dY_2}{dP}&=\frac{dB_s}{dP}+4(\tfrac{1}{3}-\Gamma)\frac{dC'}{dP}+4\Gamma\frac{dC}{dP},\\ \frac{dY_4}{dP}&=\frac{dC}{dP}+2a_1\left(\frac{dC'}{dP}-\frac{dC}{dP}\right),\\ \frac{dY_5}{dP}&=\frac{dC}{dP}+2a_2\left(\frac{dC'}{dP}-\frac{dC}{dP}\right). \end{aligned} \tag{3}$$

Taking the pressure derivative of the logarithm of any one of the equations relating the Y's to the transit times, one obtains the relation

$$\frac{1}{Y}\frac{dY}{dP}=\frac{1}{\rho}\frac{d\rho}{dP}+\frac{2}{L}\frac{dL}{dP}-\frac{2}{T}\frac{dT}{dP}. \tag{4}$$

The first two terms on the right-hand side of the equation sum to $(3B_T)^{-1}$, where B_T is the isothermal bulk modulus, and the third term is the result of the measurements on changes of transit time with pressure, that is,

$$\frac{1}{Y}\frac{dY}{dP}=\frac{1}{3B_T}-\frac{2}{T}\frac{dT}{dP}, \tag{5}$$

with all quantities to be evaluated at zero pressure. Given the zero pressure values of all the Y's and data on pressure variation of the transit times of the three waves, one can use the Eqs. (3) to compute the pressure derivatives of C, C', and B, at zero pressure. These equations determine the pressure derivatives of C and C' quite directly in the case of a [110] orientation, but the pressure derivative of B_s is derived from a combination of all three measurements.

The acoustic surface of each crystal was etched and a back reflection Laue x-ray taken after all acoustic measurements had been made. Ten spots were indexed and a least squares determination of the orientation was made.

The entire procedure outlined above was carried out for one crystal of each of silver and gold, and for two copper crystals of different lengths but similar orientation. Two copper crystals were used in order to form an estimate of the importance of any end effects such as nonhydrostatic stresses on the end of the specimen caused by differential compressibility of the quartz transducer and the metal, and possible change with pressure of acoustic end effects. The end effects proved to be less than the random experimental variations for copper, so that we felt reasonably safe in making measurements on one crystal only of each of silver and gold. These crystals just referred to were all within 2° of the [110] orientation. In addition, measurements were made on the pressure variation of the longitudinal wave transit time using a third copper crystal, near the [100] orientation.

TABLE I. Display of all pressure run data for the C_{44} shear constant for two copper crystals. The echo number is n, and the echo arrival time is T_n. T_0 is the zero-pressure transit time and R_g the pressure gauge resistance.

Crystal length (cm)	Experiment No.	n	Run No.	$\frac{-1}{nT_0}\frac{dT_n}{dR_g}$ (10^{-3} ohm^{-1})	Experiment average
			1	1.92	
			2	1.97	
	1	7	3	1.93	
			4	1.93	
			5	1.92	
1.86			6	1.91	1.93
			1	1.90	
	2	7	2	1.90	
			3	1.84	
			4	1.79	1.86
			1	1.91	
			2	1.84	
			3	2.04	
		8	4	1.93	
	1		5	2.04	
			6	1.94	
1.31			7	1.87	1.94
		8	1	2.00	
			2	1.98	1.99
	2				
			3	1.93	
		10	4	1.95	
			5	1.94	1.94

Table I gives a complete breakdown of the data taken on the pressure derivative of the C shear constant of copper, by crystal, experiment and run, several runs being shown in Fig. 1. The reproducibility is typical of these experiments; this particular shear constant has been chosen to be shown in detail in Fig. 1 and Table I because it is the one in which occurs the greatest disagreement with the previous work of Lazarus.[6]

RESULTS

The room temperature values of the elastic shear constants C, C', and the isothermal bulk modulus B_T for copper,[16] silver,[17] and gold, as used in the determination of the pressure derivatives, are given in Table II. Since the values of the zero-pressure elastic constants of gold were measured anew in the performance of this work, using a different method than the previous investigators, a comparison is shown in Table II in parentheses between the presently determined values, and the values determined by Goens[18] using the resonant bar technique. The agreement of the shear constants is especially good, but the present value of the adiabatic bulk modulus is three and one half percent higher than Goens' value. On the other hand, the present value of the bulk modulus is three percent lower than that calculated from Bridgman's[4] value of the isothermal bulk modulus ($B_T = 1.709 \times 10^{12}$ dyne cm^{-2}) by means of the equation

$$B_s \cong B_T(1+TV\beta^2 B_T/C_p), \qquad (6)$$

where β the cubical coefficient of thermal expansion equals 4.26×10^{-5} (C°)$^{-1}$ and the specific heat is $C_p = 6.03$ cal (mole−C°)$^{-1}$. V is the molar volume and T is room temperature, taken as 300°K. The value of Bridgman's B_s thus obtained is 1.77×10^{12} dyne cm^{-2}.

TABLE II. Elastic constants of copper, silver, and gold, at 25°C which were used in evaluation of the pressure derivatives of the elastic constants. Units are 10^{12} dyne cm^{-2}. The values for gold shown in parentheses for comparison are the older determination of Goens, and the recent data of Neighbours and Alers (300°K).

Metal	C	C'	B_s	B_T	Source
Cu	0.7510	0.2334	1.370	1.332	Schmunk[a]
Ag	0.4613	0.1528	1.036	1.015	Bacon and Smith[b]
Au	0.4202	0.1471	1.726	1.661	Present measurements
	(0.4202)	(0.1473)	(1.667)		Goens[c]
	(0.4195)	(0.1460)	(1.729)		Neighbours and Alers[d]

[a] See reference 16.
[b] See reference 17.
[c] See reference 18.
[d] See reference 19.

TABLE III. Pressure derivatives of the elastic constants of copper, silver, and gold. The average values shown for copper have been weighted according to the number of experiments performed.

Crystal, length, and orientation	dB_s/dP	dC/dP	dC'/dP
Cu—1.31 cm [110]	5.69	2.38	0.580
Cu—1.86 cm [110]	5.66	2.32	0.580
Cu—3.22 cm [100]	5.47	...	...
Average—Cu	5.59	2.35	0.580
Ag—1.49 cm [110]	6.18	2.31	0.639
Au—2.53 cm [110]	6.43	1.79	0.438

Also shown in Table II are very recent values for silver and gold privately communicated by Neighbours and Alers[19] who used the ultrasonic pulse-echo technique. The agreement is excellent and confirms our value of B_s for gold. We may pause to pay tribute to the work of Goens, whose shear constants for gold, obtained by an older and more difficult technique, are so well confirmed.

Table III shows the values of the pressure derivatives of the elastic constants for the silver and gold crystals and for each copper crystal measured. As already stated each entry in Table III is the result of at least two experiments and each experiment is composed of several runs.

The spread in the results obtained using several copper crystals, shown in Table III, is two percent in the case of the shear constant derivatives and four percent for the bulk modulus derivative. These figures

[16] R. E. Schmunk, M. S. thesis, Case Institute of Technology, to be submitted to Acta Metallurgica.
[17] R. Bacon and C. S. Smith, Acta Metallurgica 4, 337 (1956).
[18] E. Goens, Ann. Physik 38, 456 (1940).
[19] J. R. Neighbours and G. A. Alers, preceding paper [Phys. Rev. 111, 707 (1958)].

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felt to represent the precision of the results for the sponding measurements on each of copper, silver, gold.

e comparison of the presently determined $d\ln c/dP$ pper with the results obtained by Lazarus[6] is in Table IV. In addition, the value obtained by for the pressure variation of the shear modulus *polycrystalline* copper, $d\ln G/dP$, is listed. It will be that the Birch value, representing the derivative average shear constant, lies about midway between and C' values, but that it lies higher than both of e values as determined by Lazarus.

idgman's compressibility data are usually expressed e coefficients a and b in the equation

$$\Delta V/V_0=-aP+bP^2. \tag{7}$$

quantity a is related to the isothermal bulk modulus e equation $a=(B_T)^{-1}$ and b is related to the pres- derivative of the bulk modulus by the equation

$$b=\frac{1}{2B_T^2}\left(\frac{dB_T}{dP}+1\right). \tag{8}$$

BLE IV. Comparison of the pressure derivatives of the c shear constants of copper with previous data. Units are cm² dyne⁻¹.

Investigator	$d\ln C/dP$	$d\ln C'/dP$	$d\ln G/dP$
Present	3.13	2.48	...
Lazarus[a]	1.13	2.45	...
Birch[b]	...	...	2.76

reference 6.
reference 5.

the values of B_T given in Table II, and our values B_s/dP (adiabatic), values of b have been computed. use of dB_s/dP instead of dB_T/dP is not serious; t calculation of the difference from Eq. (6) with elp of standard thermodynamic relations shows it amounts to about 2%.)

ble V compares our values of b with the Bridgman es (as modified by Slater[20] for copper and silver). present ones are larger than the Bridgman value in se of copper, essentially the same for silver, but in the case of gold. The reason for the differences, are beyond the apparent uncertainty in our work, understood. It may be noted that in our acoustic d the quantity under discussion comes from the of a raw data plot such as Fig. 1 while in Bridg- method it comes essentially from the curvature. fact that the present result is obtained by combin- uch observations for three waves is admittedly a of the acoustic method but it is not felt to be sible for the discrepancies.

e pressure derivatives of the elastic constants of r, silver, and gold are repeated in Table VI, in rm to be used later in the interpretation of the

[20] J. C. Slater, Phys. Rev. 57, 744 (1940).

TABLE V. Comparison of present values of the pressure derivative of the bulk moduli with the Bridgman values. The values are expressed as the constant b in the equation, $\Delta V/V_0=-aP+bP^2$. Units of b are 10^{-12} cm⁴ kg⁻².

Material	Present b	Bridgman b
Cu	1.8	1.3
Ag	3.3	3.1
Au	1.3	1.8

results. That is, the pressure derivatives are expressed as $\Omega dC/d\ln r$, where the variable r may be thought of as the distance between nearest neighbor atoms of the crystal and Ω is the atomic volume. The relation between the derivative of the elastic constant c with respect to $\ln r$ and its pressure derivative is given by

$$dC/d\ln r=-3B_T(dC/dP), \tag{9}$$

and similarly for C' and B. We shall hereafter refer to the quantity $\Omega dC/d\ln r$ as the hydrostatic strain derivative of the corresponding elastic constant. The values of Ω used are: Cu 11.81, Ag 17.05, Au 16.96, in units of 10^{-24} cm³ atom⁻¹. Table VI illustrates the monotonic variation from copper to silver to gold of all these derivatives, a result to be expected of a homologous series of metals. It is felt that this good intercomparison of the three metals is additional justification of the present results in view of the discrepancies with previous workers shown in Tables IV and V.

INTERPRETATION

The elastic constants of a crystal can be expressed as the second derivative of the crystal binding energy with respect to the appropriate strain. The conventional model[21] on which elastic constant calculations are based, considers that the only important contributions to the elastic constants arise from (1) a long-range Coulomb energy, contributing to the shear constants (2) the Fermi energy, assumed in monovalent metals to be a function of volume only and consequently contributing only to the bulk modulus, and (3) a short-range repulsive interaction between neighboring closed shell ion cores. On the usual model, the short-range repulsions are considered to depend only on $|r|$, that is, they are assumed to act along lines joining nearest-neighbor atoms. In this section we shall analyze the experimental data from the point of view of this con-

TABLE VI. Hydrostatic strain derivatives, $\Omega dC/d\ln r$, of the elastic constants B_s, C, and C' of copper, silver, and gold. Units are 10^{-12} erg atom⁻¹.

Cu	Cu	Ag	Au
B_s	−264	−321	−543
C	−111	−120	−151
C'	−27.4	−33.2	−37.0

[21] N. F. Mott, in *Progress in Metal Physics*, edited by Bruce Chalmers (Interscience Publishers Inc., New York, 1952), Vol. 3, pp. 90–94.

ventional theory taken at face value, reserving comment on the detailed assumptions which will be made for the next section.

In the alkali metals, the elastic constants consist almost entirely of the long-range contributions because the ion cores are quite far apart compared to their radii. In the case of the metals copper, silver, and gold, however, the short-range contribution predominates because of the overlap of ion-core wave functions of nearest-neighbor atoms. The long-range Coulomb contributions to both shear constants as calculated by Fuchs,[22] using as a model a lattice of point charges imbedded in a uniform sea of electrons, will be called the long-range shear stiffnesses C_{lr} and C_{lr}'. The results of Fuchs are

$$\Omega C_{lr}=0.9479e^2/2a, \quad \Omega C_{lr}'=0.1058e^2/2a, \qquad (10)$$

where a is the lattice parameter, e the electronic charge, and Ω the atomic volume. The long-range contributions to the hydrostatic strain derivatives are given quite simply by

$$\Omega dC_{lr}/d\ln r=-4\Omega C_{lr}, \quad \Omega dC_{lr}'/d\ln r=-4\Omega C_{lr}'. \qquad (11)$$

The long-range contribution to the bulk modulus, which we shall call B_F, arises from the second derivative of the Fermi energy with respect to volume. For the monovalent metals, B_F is given simply by

$$\Omega B_F=\tfrac{2}{3}\bar{E}_F, \qquad (12)$$

where $\bar{E}_F$ is the average Fermi energy of the valence electrons. We shall use free electron theory with an effective mass of unity throughout this analysis. The hydrostatic strain derivative of the bulk modulus is given by

$$\Omega dB_F/d\ln r=-7\Omega B_F. \qquad (13)$$

A term arising from the first derivative of $\bar{E}_F$ with respect to r has been omitted from Eq. (12), and will be omitted consistently from expressions for bulk modulus contributions because the condition for equilibrium applies and the sum of such terms is zero. This term must be included when deriving Eq. (13), but then first derivative terms are also omitted consistently in this and subsequent expressions for contributions to the hydrostatic strain derivative of the bulk modulus. This convention accounts for the somewhat unexpected factor of 7 in Eq. (13).

These long-range contributions to the elastic stiffnesses and to their hydrostatic strain derivatives have been subtracted from the experimental values of the respective quantities in order to obtain numerical values which represent the contribution of the short-range interactions. The process is shown in detail in Table VII where it may be observed that the long-range terms are not large. In Table VII experimental stiffness values at 0°K[18,23] have been used as described in the footnote; the hydrostatic strain derivatives are for room temperature, however.

The numerical values of the short-range contributions to the stiffnesses and hydrostatic strain derivatives, obtained in this way, may now be examined in the light of the conventional model. Analytical expressions for these terms are

$$\Omega B_{sr}=\tfrac{2}{3}r^2W'', \qquad \frac{\Omega dB_{sr}}{d\ln r}=\tfrac{2}{3}(r^3W'''-3r^2W''),$$

$$\Omega C_{sr}=\tfrac{1}{2}(r^2W''+3rW'), \qquad \frac{\Omega dC_{sr}}{d\ln r}=\tfrac{1}{2}(r^3W'''+2r^2W''-6rW'), \qquad (14)$$

$$\Omega C_{sr}'=\tfrac{1}{4}(r^2W'''+7rW'), \qquad \frac{\Omega dC_{sr}'}{d\ln r}=\tfrac{1}{4}(r^3W'''+6r^2W''-14rW').$$

In these equations, W is the repulsive energy per "bond" (such that the repulsive energy per atom is $6W$ in these fcc materials with 12 nearest neighbors), and r is the nearest-neighbor spacing of the atoms. Differentiation of W with respect to r is indicated by primes, and the expressions are to be evaluated at the equilibrium value of r. The equations are written under the assumptions that the interaction W is (a) of such short range that only nearest-neighbor contributions need be considered; (b) two-body, that is, a function of $|r|$ only.[21] The entries of Table VII which are labeled short-range are presumed to be given by Eqs. (14) in the conventional theory.

At this point, there are six equations for the short-range terms, in three unknowns, rW', r^2W'', and r^3W'''. Examination of the numbers of Table VII reveals that no solutions can exist which are compatible with all equations within the variation arising from experimental error combined with uncertainties in the theoretically calculated long-range corrections. It is to be noted particularly that the long-range contributions to the hydrostatic strain derivatives are so small that the statement holds even if these contributions are neglected completely. The incompatible features of Eqs. (14) may be described in the following way: (1) the anisotropy of the short-range contributions to the shear constants, given by $\Omega C_{sr}/\Omega C_{sr}'$, is not equal

[22] K. Fuchs, Proc. Roy. Soc. (London) A153, 622 (1936); A157, 444 (1936).

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

...early equal to the anisotropy of their short-range ...ivatives; (2) the bulk modulus is in all cases too ...e in relation to the shear constants; (3) the strain ...ivative of the bulk modulus is also too large com...ed to the derivatives of the shear constants; (4) ...e conditions appear more aggravated as one pro...es down the series from copper to silver to gold. ...e failures are present regardless of the specific ...m taken for the repulsive potential, as long as the ...ential is short-range in nature so that $|r^3W'''|$ ...$r^2W''|>|rW'|$. Effects (2), (3), and (4) lead one to ...pect that the failure of conventional theory lies in ...breakdown of the assumption that W depends on $|r|$ ...y. This is, noncentral interactions could give a con...ution to the shear constants, but would not of ...se contribute to ΩB_{sr} and $\Omega dB_{sr}/d\ln r$ because the ...ter are associated with volume strain alone in which ...relative angular displacements occur.

TABLE VII. The elastic constants,[a] ΩC, and their hydrostatic ...n derivatives, $\Omega dC/d\ln r$. The experimental values, the long-...e contributions to each, and the difference between the ex...mental value and the long-range contribution to each, repre...ing the short-range contribution is shown. The units are ...erg atom^{-1}.

		Elastic constant			Hydrostatic strain derivative		
	Con-stant	Experi-ment	Long range	Short range	Experi-ment	Long range	Short range
	B	16.8	4.5	12.3	−264	−32	−232
	C	9.66	3.02	6.63	−111	−12	−99
	C'	3.03	0.34	2.69	−27.4	−1.4	−26.0
	B	18.3	3.5	14.8	−321	−24	−296
	C	8.52	2.68	5.85	−120	−11	−109
	C'	2.84	0.30	2.54	−33.2	−1.2	−32.0
	B	29.3	3.5	25.7	−543	−25	−518
	C	7.72	2.68	5.04	−151	−11	−140
	C'	2.72	0.30	2.42	−37.0	−1.2	−35.8

[a] The elastic constants used here are the values at 0°K. The copper ...s are taken from Overton and Gaffney (reference 23) and the gold ...s from Goens (reference 18). No low-temperature measurements have ...made on silver, so the Bacon and Smith values (reference 17) were ...ted to 0°K using the same fractional change which applied for the ...r and gold results. These corrections were: $C(0)/C(300)=1.084$, $C'(300)=1.091$, $B(0)/B(300)=1.036$.

The last point suggests the procedure which has ...n adopted in order to carry the analysis further. ...e assume that the radial dependence of the short-...e interaction is given by the two-parameter ex...ential potential $W=A\exp(-pr/r_0)$. The first row ...Eqs. (14) then becomes

$$\Omega B_{sr}=\tfrac{2}{3}p^2W,\quad \Omega dB_{sr}/d\ln r=-\tfrac{2}{3}(p+3)p^2W. \quad (15)$$

...e equations for the bulk modulus and its strain ...ivative serve to determine the parameters p and W ...each of the metals when the appropriate values from ...le VII are used. Numerical values for these pa...eters, describing the radial dependence of the short-...e interaction, are entered in Table VIII. The values ...the exponential parameter p for the three metals are ...n to be remarkably similar which suggests that the ...monly used exponential form is quite a good one

TABLE VIII. Values of parameters describing the short-range interactions. W is the energy per bond of the radial interaction $W=A\exp(-pr/r_0)$. Closure failures, indicated by Δ, are the amounts which must be added to conventional theory for the shear constants and their hydrostatic strain derivatives in order to obtain agreement with experiment. Units of all but p are 10^{-12} erg atom^{-1}.

Cu	Ag	Au
p	16.0	17.1	17.1
$6W$	0.43	0.46	0.79
$\Delta(\Omega C)$	−0.81	−3.28	−10.9
$\Delta(\Omega dC/d\ln r)$	26.	53.	145.
$\Delta(\Omega C')$	0.11	−0.72	−3.29
$\Delta(\Omega dC'/d\ln r)$	16.	25.	64.

over a relatively wide range of ion-core overlap. We may take as a qualitative measure of the overlap the ratio of the ionic crystal radius to the metallic atomic radius, and these are 0.75, 0.87, and 0.95 for copper, silver, and gold, respectively. The numerical values of W are also reasonable, $6W$ being about 10% of the latent heat of sublimation in each case.

The values of the exponential parameters p and W which have been obtained from the bulk modulus and its strain derivative may now be used to compute that portion of the shear stiffnesses, and of their hydrostatic strain derivatives, which arises in the radial dependence of the short-range interaction. Since we know already that the first four of Eqs. (14) will not be satisfied by the numerical values of Table VII we add to each equation a term denoted by Δ, which we call the closure failure. Thus we have

$$\begin{aligned}\Omega C_{sr}&=\tfrac{1}{2}(p-3)pW+\Delta(\Omega C),\quad \Omega dC_{sr}/d\ln r\\&=-\tfrac{1}{2}(p^2-2p-6)pW+\Delta(\Omega dC_{sr}/d\ln r),\\ \Omega C_{sr}'&=\tfrac{1}{4}(p-7)pW+\Delta(\Omega C'),\quad \Omega dC_{sr}'/d\ln r\\&=-\tfrac{1}{4}(p^2-6p-14)pW+\Delta(\Omega dC_{sr}'/d\ln r).\end{aligned} \quad (16)$$

In these equations the first term on the right results from substituting the exponential form $W=A\exp(-pr/r_0)$ in each of Eqs. (14); it can be evaluated from the values of p and W shown in Table VIII. The closure failures have been computed from Eqs. (16) using Table VII, and are entered in Table VIII. They are also shown in Fig. 2 as fractions of the corresponding total experimental quantity.

It will be observed that the closure failures, Δ, for the shear constants themselves are all negative (except for C' in copper), and range from small in copper through a large amount in silver to values in gold *which are larger than the total experimental stiffnesses themselves*. The closure failures of the hydrostatic strain derivatives are positive in sign, and increase rapidly again in the sequence copper, silver, gold but are *substantial fractions of the experimental values even for copper*. Except for the shear stiffnesses of copper, these closure terms are considerably larger than can be reasonably accounted for on the basis of experimental error or uncertainty in the theoretical long range

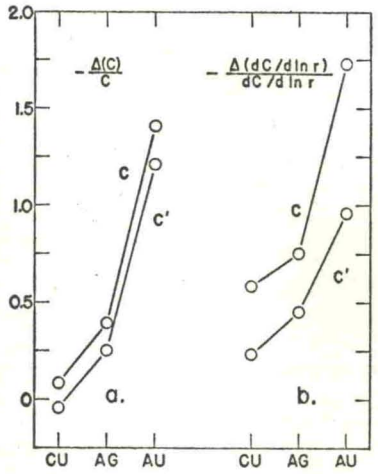

FIG. 2. Closure failures Δ expressed as fractions of the corresponding total experimental quantity. (a) Elastic shear constants; (b) hydrostatic strain derivatives of shear constants.

corrections which have been subtracted from experimental values. Since it is felt that this homologous series of metals must conform to a common model of their elastic stiffnesses and strain derivatives, we include copper in our conclusion, which is that the closure failures reflect a large, real contribution to the shear constants which is not included in the conventional theory outlined above.

We suggest furthermore that the closure failures must be assigned to many-body, noncentral, short-range interaction between metal ion cores. The absence of such an interaction is a major assumption in the conventional theory and the interaction seems to be the only way in which to account for these large discrepancies between theory and experiment for the shear constants. The ratios $-\Delta(\Omega dC/d\ln r)/\Delta(\Omega C)$ and $-\Delta(\Omega dC'/d\ln r)/\Delta(\Omega C')$ are indicative of the range of the interaction; the large values of these ratios occurring in the present results indicates that the noncentral terms are of short range indeed. It will be noted that the values of the ratios are in most cases larger than the value of p which characterizes the range of the radial part of the interaction. Further, the smoothness of the variation of the closure term from copper to gold for each constant and each strain derivative corresponds with the increasing amount of ion-core overlap and hence of the importance of the noncentral interaction in this sequence. There appears to be no theory available for the noncentral part of the many-body interaction between ion cores which has been suggested here and no *a priori* reason for or against the negative sign of the stiffness contribution which is found.

DISCUSSION

In this section we point out and discuss further the detailed assumptions involved in the analysis which was presented in the last section.

The experimental elastic constant values which have been used for the interpretation are those for the temperature of 0°K. These values are amply known, and their use enables us to avoid the difficult theoretical question of the temperature dependence of the ela[illegible] constants, and in addition we avoid the minor p[illegible] of the adiabatic-isothermal correction to the b[illegible] modulus. On the other hand, the experimental val[illegible] of the hydrostatic strain derivatives which have b[illegible] used are of necessity those for room temperature. T[illegible] analysis is somewhat inconsistent in this respect the[illegible] fore, but we do not feel that the point is important si[illegible] we expect a smaller temperature correction for t[illegible] hydrostatic strain derivatives than for the ela[illegible] constants, which itself is less than 10%. The m[illegible] direct justification for this expectation may be obtain[illegible] from the results of Bridgman on the pressure depe[illegible] ence of the bulk modulus. Bridgman's experiments ha[illegible] been carried out at two temperatures, 30°C and 75[illegible] and it is the coefficient b, in our notation, which [illegible] relevant. Inspection of Bridgman's tabulation[4] for s[illegible] forty metals shows that there is practically no cha[illegible] of b in this temperature range for most metals. Furth[illegible] more, for those metals for which there is a signifi[illegible] change, the sign is as often positive as negative. W[illegible] feel it quite probable that the hydrostatic strain deri[illegible] tives of the shear constants will also show only a sm[illegible] temperature dependence.

We have used also the hydrostatic strain derivati[illegible] of the *adiabatic* bulk modulus in our interpretation. A direct but approximate evaluation of the pressure d[illegible] rivative of $B_s - B_T$ can be made from thermodynam[illegible] and available experimental data for Cu; the result [illegible] that the pressure derivatives of B_s and B_T differ b[illegible] less than 2%. We have preferred to avoid the unc[illegible] tainty involved in this correction by using the modu[illegible] which is directly determined in the pulse-echo meth[illegible]

It has already been emphasized that the contri[illegible] tions of the long-range terms in the energy to the ela[illegible] stiffnesses and their hydrostatic strain derivatives a[illegible] small. In the interpretation they may almost be re[illegible] garded as corrections but some further discussion [illegible] worthwhile. In the conventional theory, as it has b[illegible] used in the last section, one term in the energy of t[illegible] crystal is commonly omitted in part. This term is t[illegible] energy of the lowest electronic state of the valen[illegible] electrons, which will be denoted by E_0. Physically it can be represented by the expression[24] $ar^{-3} - br^{-1}$ in which the terms represent respectively the kine[illegible] and potential energy associated with the state. In the conventional theory for the *shear* constants, E_0 appe[illegible] to a good approximation as the Coulomb stiffne[illegible] ΩC_{1r} and $\Omega C_{1r}'$ as used here.

The lowest state energy contribution to the b[illegible] modulus and its hydrostatic strain derivative has b[illegible] ignored entirely, however, and in justification of t[illegible] step the magnitudes of the derivatives E_0'' and [illegible] must be considered. The first derivative of E_0 is l[illegible] but does not enter in this analysis at all becau[illegible] equation of equilibrium has been invoked implicitly [illegible]

[24] N. F. Mott and H. Jones, *Properties of Metals and Al[illegible]* (Oxford University Press, London, 1936), p. 80.

...istently omitting first derivatives of *all* energy con-...tions. It is commonly presumed[25] that the second ...ivative E_0'' is small because the actual equilibrium ... larger than the value of r for the minimum of E_0. ...ilibrium r then occurs in the neighborhood of the ...ction point of E_0, as is shown by the available ...ulations for copper[26] and silver[27] and by the analyti... approximation given above. The contribution of ... to the bulk modulus and its hydrostatic strain ...ivative is probably small therefore. The third ...ivative E_0''' contributes to the hydrostatic strain ...ivative only; it is felt that it is also likely to be ...all in view of the fact that E_0''' is zero at a value of ...st beyond the inflection point of E_0, according to the ...lytical approximation, and hence also near the ...ilibrium value of r. Quantitative estimates of the ...sible values of $\Omega B_0 = r^2 E_0''/9$ and $\Omega dB_0/d\ln r = (rE_0''' - 3r^2E_0'')/9$ can be made by using the analyti... approximation, equating br^{-1} to the Coulomb energy ... the structure[22] and invoking the physical condition ...t $r(\text{equilibrium}) > r(E_0' = 0)$; these support the state...nts that have been made, the possible fractional ...or in the hydrostatic strain derivative being negli...le while those in the bulk modulus may be significant ...t are not serious to the conclusions of this paper.

The long-range bulk modulus which has been used ...e is then the Fermi term only, and furthermore for ...s term we have used an effective mass, m^*/m, of ...ty for all three metals. This value of the effective ...s agrees with the theoretical values of Kambe[28] ...ich characterize the electrons at the bottom of the ...ence band for copper, silver, and gold. It also ...ees with electronic specific heat effective masses[29] for ...er and gold, but not for copper in which this m^*/m ...1.47. We feel, however, that a "bulk modulus effective ...ss," which characterizes the change with volume of ... average Fermi energy, is more likely to be equal to ... theoretical value than to an effective mass de...bing the density of states at the Fermi level only.[29] ... have therefore used unity for copper also.

As mentioned above, the long-range contributions to ... shear stiffnesses which have been used are the ...lomb stiffnesses of Fuchs, and these have been ...en at their full value. Since these terms have been ...en at reduced values in other papers[2,3] in which ...tic constants have been decomposed into contribu...ns, we state our reasons. In the first place, the ...chs values have long been known to account for the shear stiffnesses of bcc Na and K,[21] and recently this has been found[30] to be true in Li also. In the alkali metals the long-range term is the major if not the only one and the agreement argues for the validity of the Fuchs calculation. There is no direct evidence for such a long-range stiffness in copper, silver, and gold but extensive studies of the elastic constants of copper[31] and silver alloys[17] in our laboratories provide good indirect evidence. The alloy results require that sizable long-range and short-range terms must both be present, and that C/C' (long range) must be about the Fuchs ratio. These two reasons lead us to regard the Fuchs values as very reasonable estimates of the long-range shear stiffness.

In some previous decompositions of elastic stiffnesses into contributions a van der Waals term has been introduced explicitly.[26] We have omitted such a term as we feel it adds nothing to the analysis which has been carried through and is a numerically uncertain contribution at best. If a contribution to the total energy of the physical nature of the van der Waals interaction is present, it is absorbed, in our treatment, in the short-range repulsive interaction $W = A \exp(-pr/r_0)$ which we have deduced empirically. Formally the van der Waals interaction is radial and of short range and cannot be separated empirically from the repulsive term.

The uncertainties in the analysis presented in the previous section thus reside almost entirely in the theoretical long-range terms. We emphasize again that these terms are small and even large individual errors would leave the conclusions unchanged. The cumulative effect of these uncertainties added to the experimental error, particularly in B and dB/dP, could be considerable, however, so that the individual numerical values of the closure failures which have been quoted and assigned to noncentral short-range interaction should be treated with caution. Nevertheless the relative values of the closure failures appear to be reasonable for the two shear constants and for the three metals.

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