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Anharmonicity in Noble Metals; Higher Order Elastic Constants*

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The third-order elastic constants of copper, silver, and gold have been measured at room temperature using high-purity single crystals. A sensitive ultrasonic interference method was employed to measure small changes of wave velocities in crystals deformed both uniaxially and hydrostatically at low stress levels. The results of the measurements were analyzed using finite elasticity theory to obtain the complete sets of six third-order constants. The values of C_{111} are largest (of the order of 10^{13} dyn/cm^2), C_{112} and C_{166} are about half of C_{111} in magnitude, and all are negative in sign. Almost all of the values of C_{123}, C_{144}, and C_{456} are negative and small compared with the other constants. It is shown that the closed-shell repulsive interaction between nearest-neighbor atoms makes the dominant contribution to the higher order elastic constants in noble metals. In this sense, the anharmonic properties are simpler than the harmonic properties of these materials. The fourth-order elastic constants are also estimated on this basis.

I. INTRODUCTION

In recent years interest in the study of the anharmonicity of crystals has increased considerably. Some examples of properties of solids which are mainly or partly determined by the crystal anharmonicity are thermal expansion, specific heat at high temperatures, thermal conductivity, temperature dependence of elastic constants, and damping of high-frequency sound waves. Anharmonicity is also of importance in the defect properties of crystals because displacements are usually large near imperfections. Many approaches have been developed for treating anharmonicity. Here we start with the continuum approach, which is primarily concerned with the nonlinearity between elastic stress and strain. Finite elasticity theory has been developed by Murnaghan,[1] who established the general stress-strain law in solids. Birch[2] treated the theory further in a form more convenient for cubic crystals. In these theories higher order elastic constants appear, which are defined as the coefficients in the expansion of the elastic strain energy of a crystal in terms of finite strains. If the higher order elastic constants are known, many anharmonic properties of the crystals can be calculated, at least on the basis of the continuum approximation. In some cases, the interaction energy between atoms can be calculated or estimated from macroscopic constants in the continuum model. For these and other reasons, it is important to determine the higher order elastic constants in crystals.

There have been a rather large number of studies of the change of the second-order (usual) elastic constants of crystals under hydrostatic pressure beginning with that of Lazarus[3] on KCl, NaCl, CuZn, Cu, and Al. Especially extensive is the work done by Smith and his co-workers on noble metals[4] and alkali halides.[5,5a] The full set of third-order elastic constants cannot, however, be obtained from hydrostatic measurements alone and other measurements, such as the change of the second-order constants in uniaxially deformed crystals, are necessary to determine the complete set. Such experiments were first performed by Hughes and Kelly[6] on isotropic materials (Pyrex glass, polystyrene, and polycrystalline iron). Bateman, Mason, and McSkimin[7] first measured the third-order elastic constants for single crystal germanium and later also for silicon using the method of analysis developed by them and by Seeger and Buck.[8] More recently, third-order constants of some alkali halide crystals (NaCl and KCl) have been obtained by Chang[9] and results for germanium, magnesium oxide, and fused silica have been given by Bogardus.[10] There have been no results on metals up to the present time because of the difficulty of the experiments. Other techniques for the determination of third-order constants have also been proposed. When ultrasonic waves proceed in an anharmonic crystal, second harmonics of the waves are generated.[11] When two ultrasonic waves interact with each other, they produce additional waves.[12] These can be used to determine the third-order constants, but complete data for metals have not yet been obtained.

It is of interest to determine the higher order elastic constants in a homologous series of metals, because the

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nature of the binding forces in metals is very different from that in ionic or covalent crystals but should be very similar in the homologous series. In the present study, the third-order elastic constants in the noble metals copper, silver, and gold have been measured at room temperature by an ultrasonic method and also the values of the fourth-order constants are estimated.

II. EXPERIMENTAL PROCEDURE

The third-order elastic constants of crystals can be determined by measuring the change of the second-order elastic constants or velocity change of ultrasonic wave velocities when the crystals are strained homogeneously by uniaxial or hydrostatic pressure. There are six independent third-order constants in cubic ($\bar{4}3m$, 432, and $m3m$ point group) crystals. Since single crystals of pure metals are usually very soft and easily deformed plastically, the applied stress must be very small. Accordingly, a sensitive method of measurement for the ultrasonic velocity change, which is usually very small when the applied stress is small, and a special technique of specimen preparation were developed. Measurements under hydrostatic pressure were also made in order to obtain more accurate results. The sensitivity of the measurements achieved was such that only as little as 60 bar of pressure was necessary.

A. Method of Measurement

A kind of ultrasonic interference method was used to measure the velocity change. When ultrasonic pulses are sent into two specimens which have the same path length but slightly different propagation-wave velocities, and the pulse echoes from the two specimens are displayed on the same oscilloscope, interference can be seen in the echo pattern. If the velocity of the wave in one specimen is further changed by a small amount, the positions of the interference nodes are shifted. It is apparent that this shift is much larger in magnitude than the shift of the individual echoes.

A Sperry ultrasonic-attenuation comparator unit was used to produce and receive the ultrasonic pulses. X-cut or AC-cut, 10-Mc/sec, quartz transducers, $\frac{1}{2}$ in. in diam, attached to the specimen faces with Nonaq stopcock grease, produce the longitudinal or transverse waves. The specimens were approximately 16-mm cubes. The volume of the specimen irradiated ultrasonically was limited by an electrode $\frac{5}{16}$ in. in diam, so that velocity changes in the nearly uniformly stressed region were measured. 10-Mc/sec fundamental waves were always used because of the rather high attenuation of the specimens at higher frequencies.

One specimen was stressed uniaxially by the loading machine or compressed hydrostatically in the pressure vessel. A Tinius Olsen loading machine with capacity of 2000 kg and an electronic controller holding the load constant was used to compress the specimen uniaxially and measure the stresses. Load readings were recorded on chart paper. The machine was calibrated by dead loads and the error was less than 0.3% of full scale in the 100-kg range. The specimen was compressed between two flat stainless-steel plates. Indium shims, 0.03 in. in thickness and 99.99% pure, were inserted between the specimen and the plates. A steel ball was put into hemispherical holes on the upper plate and pushed by the cross-head plate of the machine. In the hydrostatic measurements a pressure vessel, into which gas pressure was applied from a nitrogen tank, was made from stainless steel. The pressure could be increased and decreased by well-controlled small amounts with needle valves. A Heise Bourdon-tube pressure gauge, 150 kg/cm^2 in capacity and accurate to 0.1% of full scale, was connected to the pressure vessel.

The other specimen was set on a holder in a temperature vessel immersed in ice water. There were two heaters inside the vessel. One was large and maintained the temperature of the specimen at a nearly constant value, and the other was small and changed the temperature slightly but rather quickly. Chromel and advance thermocouple wires, 4 and 5 mil each in diam were calibrated from the ice point to room temperature against a National Bureau of Standards calibrated Pt–[Pt+Rh(10%)] thermocouple. The difference of the thermoelectromotive force of two thermocouples attached to two specimens was balanced by a Rubicon Model 2768 six-dial thermal-free potentiometer. The output of the potentiometer was connected to a Leeds and Northrup dc amplifier and recorder. The gains of the amplifier and the recorder were adjusted so that full-scale deflection of the recorder corresponded to 10-μV unbalance in the potentiometer (about 1/5°C in the temperature difference of the two specimens).

At first the temperature of the specimen in the temperature vessel was kept at a convenient point between ice and room temperature to produce the ultrasonic interference pattern, and two pulse echoes on both sides of an interference node were observed. A marker line in the oscilloscope was set to pass through the tops of these two echoes. The stress applied to the other specimen was then increased by ΔP, producing a small change of wave velocity in this specimen. The height of one echo pattern increased and the other decreased because of the shift of the interference node. Then the temperature of the specimen in the temperature vessel was changed by changing the current in the small heater until the two echoes returned back to their original heights. At this moment the change of the temperature difference of the two specimens δT was measured on the recorder chart. The speed with which the temperature of the specimen can be changed is limited by the necessity of keeping the temperature gradient in the specimen small. The wave-velocity change with stress in one specimen can be obtained if the temperature coefficient of the velocity of the other specimen is known. The uniaxial stress was usually increased up to 25–30 kg/cm^2 and again decreased in 2.5 kg/cm^2 steps in one run of the experiments, while the hydrostatic pressure was changed up to 60 kg/cm^2 in 5 kg/cm^2 steps. The temperature of the compressed specimen always drifted a small amount, but this produced almost no effect because it was only necessary to measure the temperature difference between the two specimens.

The temperature coefficient of the wave velocity was determined after each run of the compression measurement also using the interference technique. It can be shown[13] that when there is a velocity difference ΔW in two specimens, and the first interference node occurs at the nth pulse echo, $\Delta W/W_0 = 1/(2ft_0n)$, where W_0 is the reference velocity (velocity at room temperature), f is the frequency and t_0 is the time between two echoes. The temperature coefficient of the velocity $(\Delta W/W_0)/\Delta T$ can be calculated from the slope of the $1/n$ against ΔT curve, which can be obtained by changing the temperature of one specimen from the ice point to room temperature and measuring the temperature difference ΔT of the two specimens when the height of the nth echo takes on its minimum value. Some examples of such plots are shown in Fig. 1.

Finally we can obtain the velocity change by a stress increment ΔP, from the relation, $(\Delta W/W_0)/\Delta P = (\delta T/\Delta P) \times (\Delta W/W_0)/\Delta T$. The temperature difference of the specimens can be measured to 2×10^{-3}° C on the recorder chart and the temperature coefficients of the velocity of sound in metals are usually of the order of 10^{-4}°C, so that the sensitivity of the measurement of the velocity change can be as high as 10^{-7} in the optimum case. The sensitivity decreases when the attenuation of the specimen is high and only a few echoes are available. The mean value of the sensitivity we obtained was around 5×10^{-6}.

We should note here that we measured the change of the "natural velocity," which is defined as twice the path length of the specimen in the reference (undeformed) state divided by the round-trip time of waves in the final (deformed) state, because it is the change of the round-trip time that was always observed.

The positions of the interference nodes are also shifted slightly if the ultrasonic attenuation in the specimen is changed. The change of attenuation with compression was checked before each run, and it was found that the change was so small (less than 0.002 dB/μsec for the maximum stress) that the effect was negligible.

B. Preparation of the Specimens

Copper, silver, and gold specimens were supplied by Semi-Elements, Inc. according to the following specifications. Single crystals were made by the Bridgman method using 99.9995% pure materials. Two specimens which have (001), (110), and (1$\bar{1}$0) faces 15×16×17 mm in size were cut from the center part of the ingot. The accuracy of these orientations was better than $\frac{1}{3}$ degree. The specimens were chemically etched after cutting to remove the worked layer.

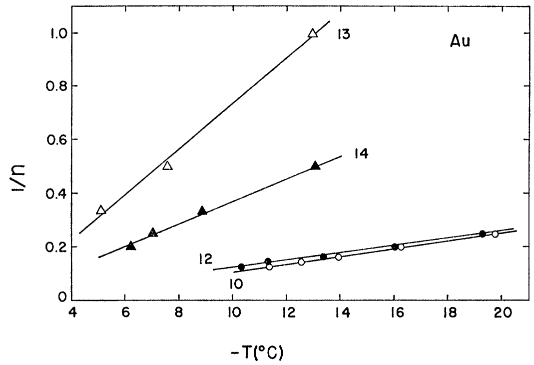

FIG. 1. Inverse of number of echoes to the first interference node $1/n$ against temperature difference between two specimens T.

The specimens were compressed in the ⟨001⟩ and ⟨110⟩ directions to a stress of 30 kg/cm^2 with the loading machine. All six faces of each specimen were then polished until the parallelness and flatness of each face were better than 5/100 000 in. The lengths between two equivalent faces in two specimens were also adjusted to be as nearly matched as possible, i.e., until no interference occurred in the pulse-echo pattern when the temperatures of the two specimens were the same. The specimens were set in a special aluminum holder and polished by hand using 2-0 and 4-0 emery paper on a flat glass plate. Parallelness and flatness were checked by an optical-lever apparatus.

Dislocations in pure metal single crystals are known to be easily movable. If this happens during the measurements, a large velocity change due to the dislocation modulus defect could occur, and the true velocity change resulting from purely elastic deformation of the lattice might not be obtained. It is well known that the apparent elastic range (range where the stress is linear with strain) is increased by prestressing the crystal, probably as a result of the tangling or interaction of many dislocations produced by the plastic deformation. Further plastic deformation continues when the stress is again increased above the prestress level. Similar behavior can be seen in the velocity change against stress curves in Fig. 2. The velocity change is almost linear until the stress approaches the prestress value, after which drastic changes occur above the prestress level. If the prestress level was increased, the linear range was extended to the new prestress value. It may be supposed that no over-all movement of dislocations occurs below the prestress level. Usually, measurements were carried out in such a range of stresses. Sometimes there are deviations from linearity in the initial part of a run (low stress part for increasing stress runs and high stress part for decreasing stress runs). These may

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[13] R. P. Espinola and P. C. Waterman, J. Appl. Phys. 29, 718 (1958).

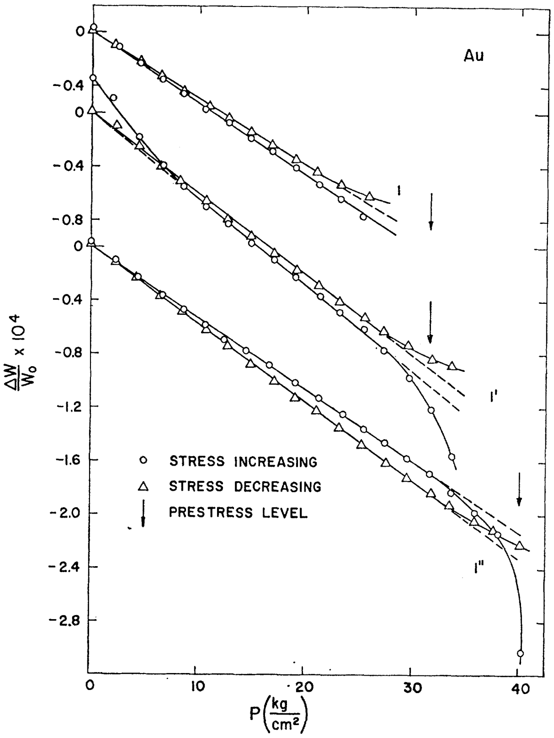

FIG. 2. Velocity change with uniaxial stress below and above the prestress level.

be due to the defect modulus change by depinning of dislocations from point defects, which should disappear when all breakable pinning points are exhausted.

III. RESULTS

A. Experimental Data

Nine uniaxial and five hydrostatic measurements were carried out for each material with various directions of compressing the specimens using various propagation and polarization directions of the ultrasonic waves (Table I). The results are gathered in Figs. 3–8.

TABLE I. Fourteen sets of measurements used.

No.	Direction of compression	Direction of propagation	Direction of polarization
1	001	110	110
2	001	110	$1\bar{1}0$
3	001	110	001
4	110	001	001
5	110	001	110
6	110	001	$1\bar{1}0$
7	110	$1\bar{1}0$	$1\bar{1}0$
8	110	$1\bar{1}0$	110
9	110	$1\bar{1}0$	001
10	all	001	001
11	all	001	110
12	all	110	110
13	all	110	$1\bar{1}0$
14	all	110	001

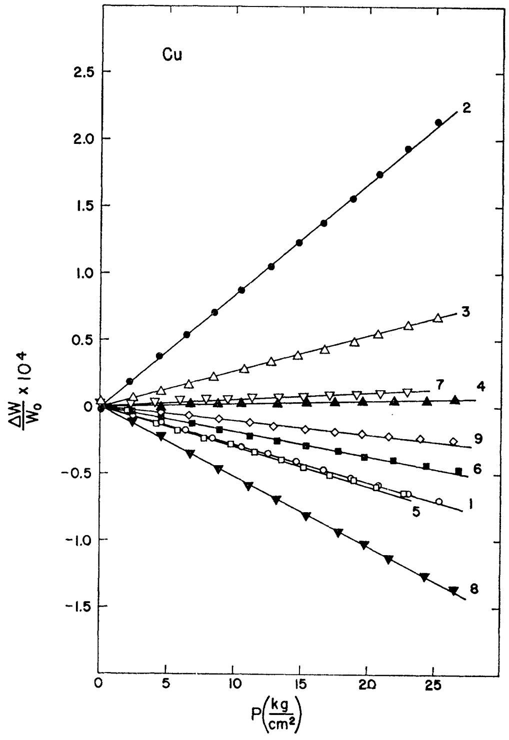

FIG. 3. Velocity change with uniaxial stress in copper.

The numbers attached to these curves are those which appear in the first column in Table I. In the case of gold, the change was so small for case 7 that the slope

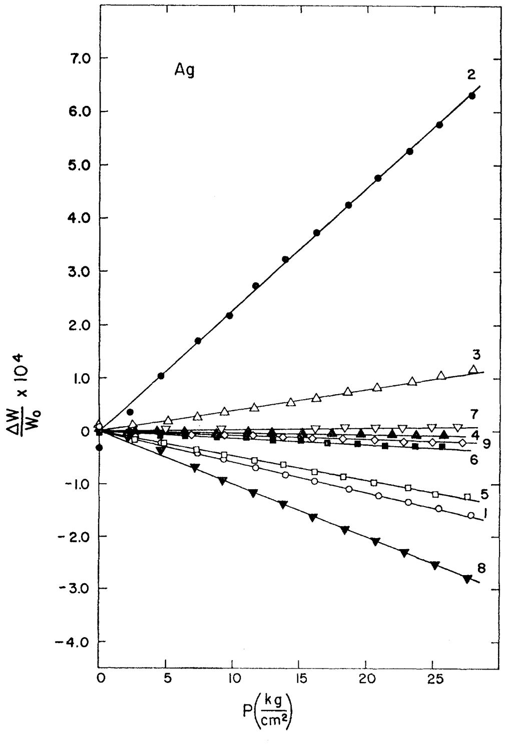

FIG. 4. Velocity change with uniaxial stress in silver.

could not be determined with sufficient accuracy to be included. Straight lines fitting the data points were determined by the least-mean-square method, the values of $\Delta W/W_0$ being shifted so that the lines passed through the origin. Some points which apparently deviate from linearity were omitted to determine the lines. Each measurement was made with both increasing and decreasing stresses. Only the decreasing stress runs are shown in the Figs. 3–8 for the purpose of clarity in the figures.

The slopes of the lines for increasing and decreasing stresses are sometimes slightly different, as can be seen in Fig. 2. This may be partly due to a small contribution from dislocation movement, and partly to the measuring method because the differences, although smaller than those in the uniaxial cases, also exist in the hydrostatic case where dislocations should be unaffected. Non-uniformity in the temperature and the stresses in the specimens may be the main sources of the errors. Irregularities are seen in the points near the origin which are rather large in the hydrostatic cases. These may be the effect of changes of thickness with pressure of the adhesive material between the specimen and the transducer. The difference between the slopes of curves 11 and 14, which should be equivalent, is reduced when the mean value of the slope for both increasing and decreasing pressure is used.

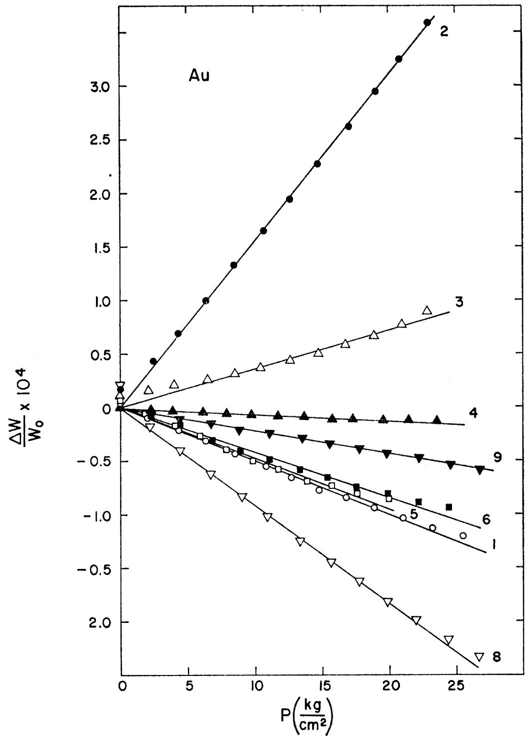

FIG. 5. Velocity change with uniaxial stress in gold.

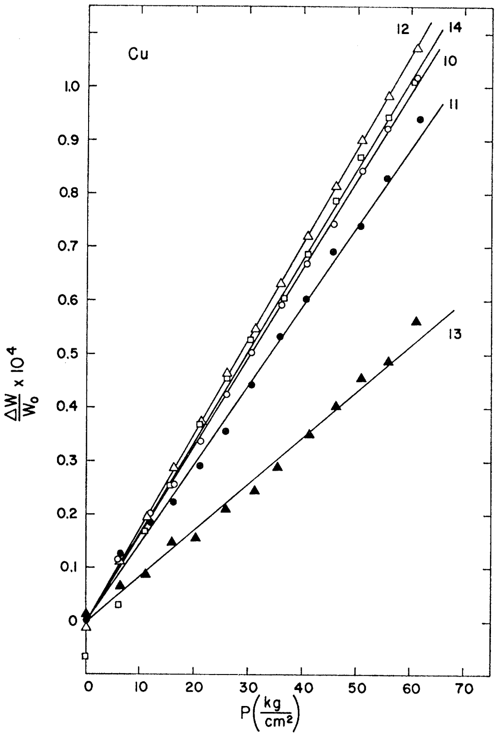

FIG. 6. Velocity change with hydrostatic pressure in copper.

The adiabatic second-order elastic constants were also measured at room temperature by the usual ultrasonic technique. The results are shown in Table II

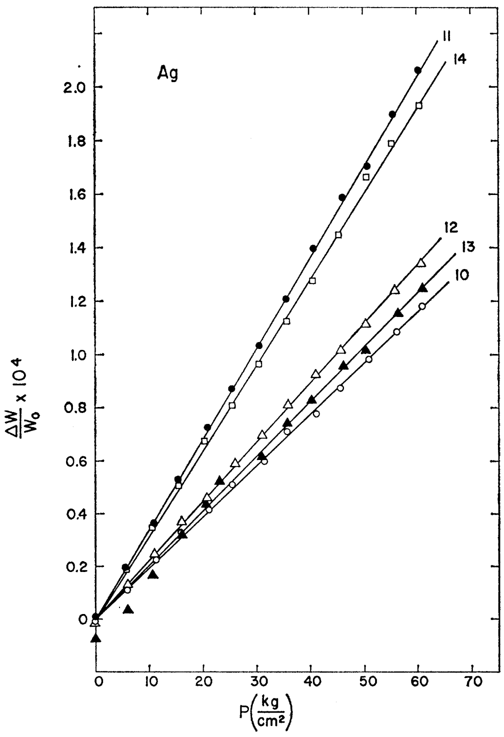

FIG. 7. Velocity change with hydrostatic pressure in silver.

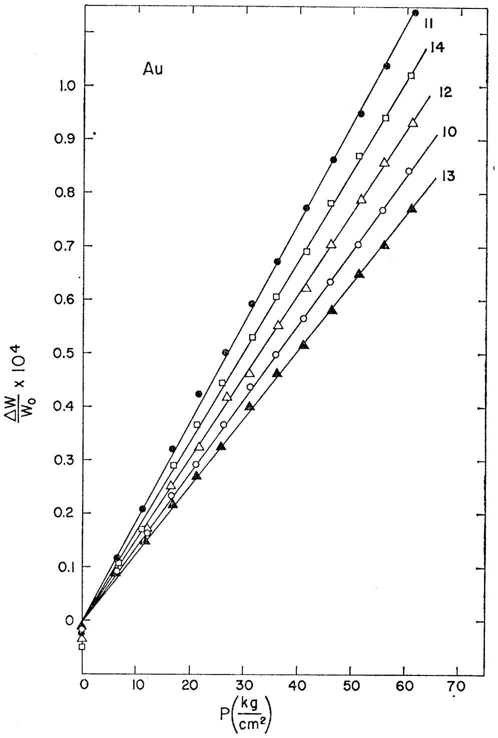

FIG. 8. Velocity change with hydrostatic pressure in gold.

together with the data by other authors on Cu,[14] Ag, and Au.[15] These quantities were not of primary interest in the present experiments, but the agreement is seen, nevertheless, to be good.

B. Analysis of the Data

Third-order elastic constants of the three materials have been calculated by analyzing the data of the velocity changes with stress. When the elastic energy of the crystal is expanded in a series of strains, elastic constants are defined as the coefficients of the terms of the series.[2] Here we follow the definitions of Brugger,[16] who defines the adiabatic and the isothermal nth order elastic constants as

$$c^S{}_{jkpq\cdots}=\rho_0(\partial^n U/\partial\eta_{jk}\partial\eta_{pq}\cdots)_S\,,$$
$$c^T{}_{jkpq\cdots}=\rho_0(\partial^n F/\partial\eta_{jk}\partial\eta_{pq}\cdots)_T\,, \qquad (1)$$

where U and F are the internal energy and the free energy per unit mass of crystal, S and T are the entropy and the temperature, and ρ_0 is the density of the crystal in the undeformed state. The η_{jk}'s are the Lagrangian strain components:

$$\eta_{ij}=\frac{1}{2}\left(\frac{\partial x_k}{\partial a_i}\frac{\partial x_k}{\partial a_j}-\delta_{ij}\right), \quad (i,j,k=1,2,3)\,, \qquad (2)$$

where a_i and x_i are the Cartesian components of a material particle in the unstrained and strained states. Summation over all repeated indices is hereafter always implied.

TABLE II. Second-order adiabatic elastic constants in copper, silver, and gold (in 10^{12} dyn/cm^2).

	Cu	Ag	Au	Author
c_{11}	1.661	1.222	1.929	Present
	1.684	1.240	1.923	a, b
c_{12}	1.199	0.907	1.638	Present
	1.214	0.937	1.631	a, b
c_{44}	0.756	0.454	0.415	Present
	0.754	0.461	0.420	a, b

[a] Reference 14.
[b] Reference 15.

The changes of the apparent second-order elastic constants ρV^2, where ρ and V are the density and the velocity of sound in the deformed crystal, with stress, can be calculated from the finite elasticity theory.[7,8] The density and the path length are, however, also changed by stresses, and they must be properly corrected to calculate the third-order constants. A convenient method of analysis was developed by Thurston and Brugger[17,18] by solving the equations of small-amplitude waves in a homogeneously deformed crystal. They calculated the change of the quantity $\rho_0 W^2$ with stress p where ρ_0 is the density of the crystal in the undeformed state and W is the "natural velocity," both of which can be directly obtained from the measurements. The general expressions are

$$-[\partial(\rho_0 W^2)/\partial p]_{p=0}=(\mathbf{N}\cdot\mathbf{M})^2+2wF+G\,,$$
$$w=(\rho_0 W^2)_{p=0}=c^S{}_{prqs}N_pN_qU_rU_s\,,$$
$$F=s^T{}_{abrs}M_aM_bU_rU_s\,,$$
$$G=s^T{}_{abuv}C_{uvprqs}M_aM_bN_pN_qU_rU_s\,, \qquad (3)$$

for uniaxial stress. c^S and s^T are the second-order isentropic stiffnesses and isothermal compliances, and the third-order stiffnesses C are isothermal strain derivatives of isentropic second-order stiffnesses. These are evaluated at the undeformed state of the crystal. **M**, **N**, and **U** are the unit vectors along the direction of stress, direction of propagation, and polarization of the waves in the absence of the static stress. The formulas for the hydrostatic case can be obtained by putting $(\mathbf{N}\cdot\mathbf{M})=1$, $M_a=M_b=1$, and $a=b$. A linear combination of third-order elastic constants G can be obtained by measuring the change of the natural velocity with stress and using the values of the second-order elastic constants in the undeformed state. The explicit expressions for the cases of pure mode waves in a cubic crystal are given in their paper.[17]

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

[15] J. R. Neighbours and G. A. Alers, Phys. Rev. **111**, 707 (1958).

[16] K. Brugger, Phys. Rev. **133**, A1611 (1964).

[17] R. N. Thurston and K. Brugger, Phys. Rev. **133**, A1604 (1964).

[18] K. Brugger, J. Appl. Phys. **36**, 768 (1965).

We determined six third-order elastic constants in each material using 14 sets of measurements, nine uniaxial and five hydrostatic cases and increasing and decreasing stress runs for each of them. A weighted least-mean-square method was used to obtain the most probable values and their probable errors. The hydrostatic measurements were considered to be more reliable than the uniaxial ones because of the absence of difficulties such as dislocation movement or nonuniformity of the stresses in the specimens. The internal consistency among the different measurements was at first checked. There are some identities between G's in Eq. (3) when they are applied to the simple cases we used for measurements, namely,

$$G_1+G_2+G_3=G_4+G_5+G_6,$$

and $G_6=G_9$ for the uniaxial cases and

$$G_{10}+G_{11}=G_{12}+G_{13},$$

and $G_{11}=G_{14}$ for the hydrostatic cases where the suffixes are the numbers in the first column in Table I.

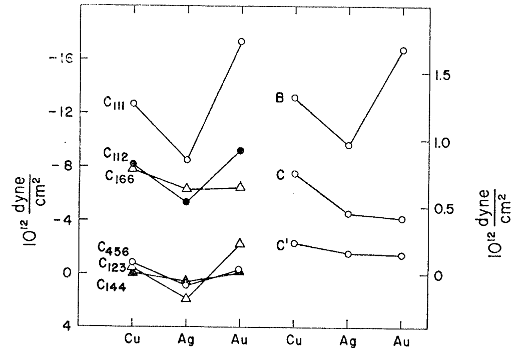

FIG. 9. Second- and third-order elastic constants in copper, silver, and gold.

The percentage deviations of the measured values from these identities

$$[\text{e.g., } 100\times|(G_1+G_2+G_3)-(G_4+G_5+G_6)|/(G_1+G_2+G_3+G_4+G_5+G_6)]$$

were 16.1, 9.9 and 15.0% for Cu, Ag, and Au in uniaxial cases and 3.6, 1.5, and 1.4% in hydrostatic cases for the mean values of the two identities. Different weights inversely proportional to the above values were put in for uniaxial and hydrostatic measurements, respectively. Each measurement is also considered to be more accurate when the difference of the two values of G's for increasing and decreasing stress runs is small, and different weights were given to each of the measurements. The mean values of the percentage differences of the two G's were 4.2, 7.4, and 5.6% for Cu, Ag, and Au in the uniaxial cases and 1.8, 0.8, and 0.9% in hydrostatic cases.

The final results are tabulated in Table III. The probable errors found are comparable to those obtained in the earlier work on germanium.[7] These values are plotted in Fig. 9 together with three independent second-order elastic constants $B=\frac{1}{3}(c_{11}^T+2c_{12}^T)$, $C=c_{44}^T$, and $C'=\frac{1}{2}(c_{11}^T-c_{12}^T)$. It is interesting to note that regular changes of these constants are seen in the homologous series of noble metals.

TABLE III. Third-order elastic constants in copper, silver, and gold (in 10^{12} dyn/cm^2).

	Cu	Ag	Au
C_{111}	-12.71 ± 0.22	-8.43 ± 0.37	-17.29 ± 0.21
C_{112}	-8.14 ± 0.09	-5.29 ± 0.18	-9.22 ± 0.12
C_{123}	-0.50 ± 0.18	$+1.89\pm0.37$	-2.33 ± 0.49
C_{144}	-0.03 ± 0.09	$+0.56\pm0.26$	-0.13 ± 0.32
C_{166}	-7.80 ± 0.05	-6.37 ± 0.13	-6.48 ± 0.17
C_{456}	-0.95 ± 0.87	$+0.83\pm0.08$	-0.12 ± 0.16

C. Comparison with Other Experiments

No other data are available at the present time with which to compare the complete set of third-order elastic constants in metals. There have been studies of the changes of the second-order elastic constants of noble metals under hydrostatic pressure.[3,4] The results are summarized in Table IV together with our values which were obtained from our data of the velocity changes under pressure after correcting for changes of density and path length with pressure by the usual method.[4] In some cases discrepancies are seen in these data, but they are not systematic. Our values were calculated from five independent measurements for one specimen and the internal consistency between these five measurements was very good. The main difference in the three experiments is that both Lazarus and Daniels and Smith measured values up to 10 000 bar while the pressure range is very low in our case (60 bar at maximum pressure). An advantage in working at low pressures is that no attenuation changes occur during the pressure cycling. For the high pressure (to 10 000

TABLE IV. Pressure derivatives of second-order elastic constants of copper, silver, and gold.

	Cu	Ag	Au	$p_{\max}$(atm)	Author
dC/dp	2.63	3.04	1.52	60	Present
	0.83	···	···	10^4	a
	2.35	2.31	1.79	10^4	b
dC'/dp	0.375	0.755	0.380	60	Present
	0.566	···	···	10^4	a
	0.580	0.639	0.438	10^4	b
dB/dp	5.44	4.11	5.21	60	Present
	3.91	···	···	10^4	a
	5.59	6.18	6.43	10^4	b
	5.3	5.1	4.6	3×10^4	c
	4.1	4.5	5.5	5×10^5	d
	4.8	5.6	5.2	4×10^6	e

[a] Reference 3.

[b] Reference 4.

[c] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **77**, 187 (1949).

[d] M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid State Physics*, Vol. 6, p. 1 (Academic Press Inc., New York, 1958).

[e] L. V. Al'tshuler, K. K. Kruprikov, B. N. Ledenev, V. I. Zhuchikhim, and M. I. Brazhnik, Zh. Eksperim. i Teor. Fiz. **34**, 874 (1958) [English transl.: Soviet Phys.—JETP **7**, 606 (1958)].

bars) experiments, it was found that the difference in compressibility between the quartz and the specimens stresses the specimens sufficiently to change the attenuation and even to shatter the quartz transducer each time a set of pressure runs is made. The values listed for dB/dp in the last three rows of Table IV are derived by differentiation of pressure-volume data at very high pressures. There seems to be no systematic trend.

IV. DISCUSSION

The elastic constants of a crystal at zero temperature can be calculated when the energy density of the crystal is known as a function of the elastic strains. In the case of typical alkali halide crystals, the Born model of ionic solids can be adopted as a good approximation. The total energy of the crystal can be obtained by summing up the interaction energy between ions, using the Born-Mayer potential and the Coulomb potential as the short-range repulsive and the long-range attractive contributions. These potentials are functions of the ion separation which can be expressed in terms of the strains in the crystal. In this way, one can calculate the elastic constants of any order. Several authors[19–21] have calculated the third-order elastic constants in NaCl-type and CsCl-type crystals, obtaining fair agreement with the (incomplete) data available so far.[21]

The situation is more complicated in metals. It is closely related to the problem of calculating the cohesive energy of metals, and the aspects are different in metals of different kinds. Fuchs[22] treated the cohesion of monovalent noble metals (Cu) using the method of Wigner and Seitz,[23] and calculated the second-order elastic constants of Cu and also of alkali metals (Li, Na, and K). According to his method the total energy of the lattice is divided up for convenience into the following terms: the kinetic energy in the lowest electronic state, the Fermi energy of the electrons, the potential energy between ion-ion, electron-electron, and ion-electron pairs, the van der Waals energy between the ions, and the exchange energy due to the overlapping of the closed shells of the ions. The noble metals Cu, Ag, and Au differ from the alkali metals in that the closed d shells overlap much more than do the closed p shells of the alkalis. The exchange-repulsion term does not contribute much to the total lattice energy, but it makes a major contribution to the elastic constants. For example, the contribution of the exchange repulsion to the shear constants $\frac{1}{2}(c_{11}-c_{12})$ is about eight times that from the electrostatic energy of the valence electrons and ions in the case of Cu, but the former is only one part in 70 of the latter in the case of Na.[24]

The contribution of the closed-shell repulsive term becomes more and more predominant in the higher order elastic constants in the noble metals. When the total energy of the crystal is expressed as a function of the interatomic separation r, the energy has a minimum at the equilibrium separation r_0. The total energy of noble metals can be separated into two terms: the interaction energy between closed shells U_c and the energy from all other sources U_e. The latter changes slowly and monotonically with r near the equilibrium position $r=r_0$ in the case of the noble metals.[25] It may be reasonably assumed that U_e also changes slowly and monotonically with homogeneous relative displacements of the atoms. Then we can expand U_e in a power series of the strains of the crystals η_{ij} and the expansion coefficients become expansion. The energy U_c can meanwhile be treated as the sum of repulsive energy terms between ions $w(r)$, which are of an additive, short-range, two-body, central force type.

The total energy of the crystal per unit volume $U=U_c+U_e$ can then be expressed as

$$
\begin{aligned}
U=&(1/2V_0)\sum w(r)\\
&+f_0+f_1(\eta_{11}+\eta_{22}+\eta_{33})+f_2(\eta_{12}+\eta_{23}+\eta_{31})\\
&+f_{11}(\eta_{11}^2+\eta_{22}^2+\eta_{33}^2)+f_{12}(\eta_{11}\eta_{22}+\eta_{22}\eta_{33}+\eta_{33}\eta_{11})\\
&+f_{44}(\eta_{12}^2+\eta_{23}^2+\eta_{31}^2)+f_{111}(\eta_{11}^3+\eta_{22}^3+\eta_{33}^3)\\
&+f_{112}\{\eta_{11}^2(\eta_{22}+\eta_{33})+\eta_{22}^2(\eta_{33}+\eta_{11})+\eta_{33}^2(\eta_{11}+\eta_{22})\}\\
&+f_{123}(\eta_{11}\eta_{22}\eta_{33})+f_{456}(\eta_{12}\eta_{23}\eta_{31})\\
&+f_{144}(\eta_{11}\eta_{23}^2+\eta_{22}\eta_{31}^2+\eta_{33}\eta_{12}^2)\\
&+f_{166}\{\eta_{12}^2(\eta_{11}+\eta_{22})+\eta_{23}^2(\eta_{22}+\eta_{33})+\eta_{31}^2(\eta_{33}+\eta_{11})\}\\
&\qquad\qquad+f_{1111}(\eta_{11}^4+\eta_{22}^4+\eta_{33}^4)+\cdots,
\end{aligned}
\tag{4}
$$

where V_0 is the volume of the elementary cell, $w(r)$ is the energy per ion pair, η_{ij}'s are the strains defined in Eq. (2), and the f's are constants. The difference of the square of the separation of two material particles in the deformed and undeformed states is[21]

$$
r^2-r_0^2=2\sum_{\alpha\beta}\xi_\alpha\xi_\beta\eta_{\alpha\beta},\quad(\alpha,\beta=1,2,3),
\tag{5}
$$

where ξ_α is the difference of the Cartesian coordinates of the particles in the undeformed state, and

$$
\frac{\partial}{\partial\eta_{\alpha\beta}}=\xi_\alpha\xi_\beta\frac{1}{r}\frac{d}{dr}=\xi_\alpha\xi_\beta D.
\tag{6}
$$

The elastic constants can be obtained by the definition in Eq. (1):

$$
c_{ijkl}=(\partial^2U/\partial\eta_{ij}\partial\eta_{kl})_{r=r_0},
\tag{7}
$$

$$
C_{ijklmn}=(\partial^3U/\partial\eta_{ij}\partial\eta_{kl}\partial\eta_{mn})_{r=r_0},
\tag{8}
$$

$$
C_{ijklmnop}=(\partial^4U/\partial\eta_{ij}\partial\eta_{kl}\partial\eta_{mn}\partial\eta_{op})_{r=r_0},
\tag{9}
$$

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[24] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, England, 1936), p. 149.

[25] See, for example, Fig. 58 on p. 145 of Ref. 24.

and there is no difference between the isothermal and adiabatic constants because we are considering the values at zero temperature. These constants are (expressed in the contracted notation):

$$c_{11}=(1/2V_0)\sum \xi_1{}^4[D^2w]_{r=r_0}+2f_{11},\quad \text{etc.,} \tag{7a}$$

$$C_{111}=(1/2V_0)\sum \xi_1{}^6[D^3w]_{r=r_0}+6f_{111},\quad \text{etc.,} \tag{8a}$$

$$C_{1111}=(1/2V_0)\sum \xi_1{}^8[D^4w]_{r=r_0}+24f_{1111},\quad \text{etc.} \tag{9a}$$

If only the nearest-neighbor interaction is taken for the repulsive term and the values of all twelve sets of values of ξ's ($\xi_1=r_0/\sqrt{2}$, $\xi_2=r_0/\sqrt{2}$, $\xi_3=0$, etc.) are summed up, one obtains

$$\begin{aligned} c_{11}&=(r_0{}^4/V_0)[D^2w]_{r=r_0}+2f_{11},\\ c_{12}&=(r_0{}^4/2V_0)[D^2w]_{r=r_0}+f_{12},\\ c_{44}&=(r_0{}^4/2V_0)[D^2w]_{r=r_0}+2f_{44}, \end{aligned} \tag{7b}$$

$$\begin{aligned} C_{111}&=(r_0{}^6/2V_0)[D^3w]_{r=r_0}+6f_{111},\\ C_{112}&=(r_0{}^6/4V_0)[D^3w]_{r=r_0}+2f_{112},\\ C_{123}&=f_{123},\\ C_{456}&=f_{456},\\ C_{144}&=2f_{144},\\ C_{166}&=(r_0{}^6/4V_0)[D^3w]_{r=r_0}+2f_{166},\\ &\text{(etc., for higher orders).} \end{aligned} \tag{8b}$$

If f_{11}, f_{12}, and f_{44} are omitted in Eq. (7b), the relations $c_{11}=2c_{12}=2c_{44}$ are obtained. These are far from satisfied in noble metals (Table II); that is, it is necessary to know the contributions from U_e to calculate the second-order elastic constants. When the f's are omitted, the relations for the third-order constants become

$$\begin{aligned} C_{111}&=2C_{112}=2C_{166},\\ C_{123}&=C_{456}=C_{144}=0. \end{aligned} \tag{10}$$

The measured values are more closely described by these relations (Table III) than is the case for the second-order constants, which means that the closed shell repulsive contribution becomes more predominant in the third-order constants than in the second-order constants. Milder relations (Cauchy relations for the third-order constants) hold generally for the central force case: $C_{112}=C_{166}$ and $C_{123}=C_{144}=C_{456}$. These seem to be well satisfied, especially in the case of Cu, which shows that a central-force-type interaction makes the dominant contribution to the third-order elastic constants, at least in Cu. Such relations should be checked at zero temperature, but the temperature dependence of the elastic constants would not be expected to be large enough to modify this tendency very much.

It may be a good approximation to use only the repulsive term for the fourth-order elastic constants. There are 11 fourth-order constants in cubic crystals.[26] By the same argument, we obtain the relations

$$\begin{aligned} C_{1111}&=2C_{1112}=2C_{1122}=2C_{1155}=2C_{1266}=2C_{4444},\\ C_{1123}&=C_{1144}=C_{1255}=C_{1456}=C_{4455}=0. \end{aligned} \tag{11}$$

These relations are useful in estimating these constants because direct measurements of the fourth-order constants in the usual way may be difficult, if not impossible, at the present time.

We may proceed further by assuming a Born-Mayer-type potential

$$w(r)=A\exp[-B(r/r_0-1)] \tag{12}$$

for the repulsive term. Using Eq. (8b) and similar formulas for the fourth-order constants and omitting the terms from other than the repulsive closed-shell interaction, we obtain

$$C_{111}=-AB(B^2+3B+3)/2V_0, \tag{13}$$

$$C_{1111}=AB(B^3+6B^2+15B+15)/4V_0. \tag{14}$$

The ratio of the two elastic constants depends only on the "hardness" constant B. Mann and Seeger have estimated the values of the parameters A and B in noble metals semiempirically in several different ways.[27] Their value of B varies from 12 to 24 for Cu, Ag, and Au according to the methods and parameters which appear in each method. Using Eqs. (13) and (14) the ratio of fourth- order to third-order constants can then be estimated as $-C_{1111}/C_{111}=7$–14. Thus, the fourth-order constant is positive in its sign and several times larger than the third-order constants.

In conclusion, the assumption that the ion core repulsive term contributes predominantly to the higher order elastic constants of noble metals seems to give a fair account of the measured values. It may be interesting to measure the third-order constants in noble metals alloyed with divalent elements to study the contribution from the valence electrons. Also interesting would be measurements of the higher order constants in metals such as aluminum, the ionic radius of which is much smaller than that of noble metals so that the ion-ion core repulsion may not predominate over other terms.

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