PHYSICAL REVIEW VOLUME 111, NUMBER 3 AUGUST 1, 1958

Elastic Constants of Silver and Gold

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(Received March 4, 1958)

The three elastic constants C_{44}, $\frac{1}{2}(C_{11}-C_{12})$, and $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ have been directly measured for silver and gold in the temperature range between 4.2 and 300°K. The various contributions to the values of the 0°K constants are analyzed in terms of a simple model which quite successfully describes copper. It is concluded that such a model is unsatisfactory when applied to the heavier noble metals because these appear to have large noncentral forces contributing to their constants. Combined with pressure data the present results show the elastic constants to be explicit functions of temperature. The Debye characteristic temperatures calculated from the 0°K elastic constants are shown to be in substantial agreement with the results from calorimetry.

INTRODUCTION

IN addition to being of interest as intrinsic physical properties, the elastic constants of a solid give information concerning the nature of the forces operating in solids. Measurements on single crystals at liquid helium temperatures are most important since they are readily comparable to theory. The composite oscillator technique has been used at liquid nitrogen temperatures on sodium[1] and aluminum.[2] Dyanmic bending and torsion measurements down to the liquid hydrogen range have been performed on crystals of copper, gold, lead, and aluminum by Goens.[3] Quite recently the pulse method has been used to investigate copper[4] and zinc[5] from room temperature to the liquid-helium range. The semiempirical calculations by Fuchs[6] of the elastic constants of sodium, potassium, and copper are essentially in agreement with these experiments. Measurements on the heavier noble metals are needed to afford a further test of these calculations.

The low-temperature elastic constants may also be used to calculate the Debye characteristic temperature at 0°K which is required for the proper analysis of low-temperature specific-heat measurements. However, there exist so few elastic-constant measurements at liquid helium temperature that the various methods of calculating θ_D from elastic data cannot be critically examined in order to determine the extent to which they can be trusted in the analysis of specific-heat results. In accordance with these views an investigation of the elastic constants of silver and gold in the temperature interval 4.2°K to 300°K was undertaken.

Experimental Procedure

Silver and gold single crystals were prepared by a modified Bridgman method in a manner similar to that previously described[7]; the metal being contained in a carbon crucible which was heated and cooled slowly in an argon atmosphere resistance furnace. After removal from the crystal growing furnace, the ingots were etched and mounted in a jig. Back reflection Laue photographs were used to align the jig so that a [110] direction in the ingot was parallel to the x-ray beam. A cylinder with faces normal to [110] was then cut out of each ingot with a thin liquid-cooled abrasive wheel. These single-crystal cylinders were then hand-lapped until the faces were flat and parallel to within ±0.0004 cm. The length of the resulting [110]-oriented single-crystal cylinders measured 1.4548 cm for silver and 1.6261 cm for gold. Spectrographic analyses of portions of the single-crystal ingots showed them to be of higher purity than the Matthey spectrographic standards.

Determination of the wave velocities was by a modified pulsed ultrasonic method.[5] In this arrangement, the 10-Mc/sec pulses are displayed without passing through a detector stage, and the time between echoes was determined by direct comparison with standard time markers simultaneously displayed on the oscilloscope. Attenuation in both silver and gold is small enough so that it was possible to obtain echo trains lasting for several hundred microseconds. Individual settings were reproducible to ±0.01 μsec.

For temperature control, the specimen was mounted on a flat copper plate which was placed in a copper can covered with Styrofoam insulation. A heater coil, resistance thermometer, and copper-constantan thermocouple were attached to the plate. Two thin brass rods served as supports for the plate and provided a slight thermal contact with the bath of either liquid nitrogen or helium. A Brown Electronik Recorder was used to control and measure the temperature of the copper plate and hence the specimen. The thermocouple was used for determining temperatures above 77°K and the resistance thermometer below. The resistance-temperature characteristics of the thermometer were taken from the measurements of Dauphinee and Preston-Thomas.[8] Over the entire range the temperature could

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[1] S. L. Quimby and S. Siegel, Phys. Rev. **54**, 293 (1938).
[2] P. M. Sutton, Phys. Rev. **91**, 816 (1953).
[3] E. Goens, Ann. phys. **38**, 456 (1940).
[4] W. C. Overton and J. Gaffney, Phys. Rev. **98**, 969 (1955).
[5] G. A. Alers and J. R. Neighbours (to be published).
[6] K. Fuchs, Proc. Roy Soc. (London) **A153**, 622 (1936).
[7] Neighbours, Bratton, and Smith, J. Appl. Phys. **23**, 389 (1952).
[8] T. M. Dauphinee and H. Preston-Thomas, Rev. Sci. Instr. **25**, 885 (1954).

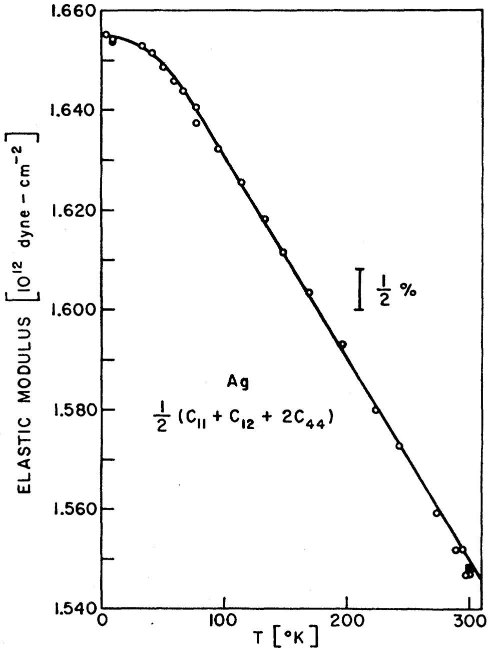

FIG. 1. The adiabatic elastic constant $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ for silver as a function of temperature. The black square marks the room temperature result of Bacon.

be measured to better than 0.1 degree and could be controlled to at least 0.5 degree over the time required for a measurement.

Longitudinal and transverse acoustic waves were generated by X cut and B-T cut quartz transducers with Salol as a binder at room temperature. At all other temperatures glycerin was used. As discussed previously,[5] it is felt that no transit time correction is justifiable. The density used in computing the elastic constants was taken from the ASTM powder x-ray card file. These room temperature densities, for gold $\rho=19.30$ g/cm^3 and for silver $\rho=10.50$ g/cm^3, and the measured values of the sound velocity, V, were corrected for thermal expansion by using the expansion coefficient data of Nix and McNair.[9] The experimental results are then a list of ρV^2 values as a function of temperature.

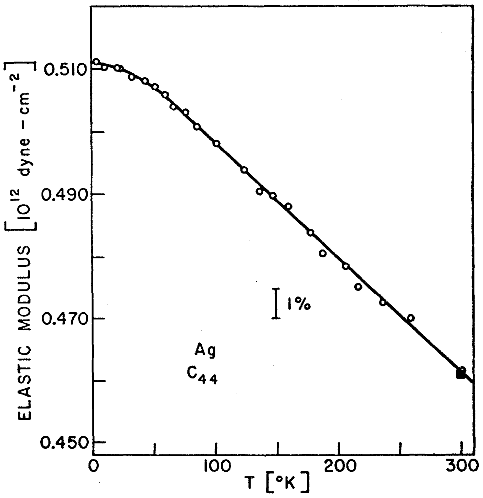

FIG. 2. The adiabatic elastic shear constant C_{44} for silver as a function of temperature. The black square marks the room temperature result of Bacon.

RESULTS

From determination of the elastic wave velocities in a [110]-oriented cubic crystal, one obtains directly three independent linear combinations of the elastic constants. These directly determined quantities, C_{44}, $\frac{1}{2}(C_{11}-C_{12})$, and $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$, are shown in Figs. 1–6 and are sufficient to define all the elastic constants. Figures 1 and 4 show the quantity $\rho V_1^2=\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ plotted as a function of temperature for silver and gold. Figures 2 and 5 show $\rho V_2^2=C_{44}$ and Figs. 3 and 6 show $\rho V_3^2=\frac{1}{2}(C_{11}-C_{12})$ plotted as a function of temperature.

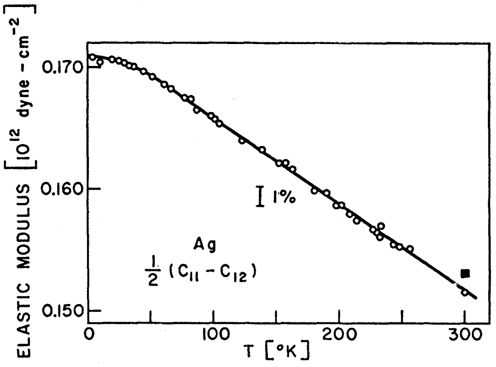

FIG. 3. The adiabatic elastic shear constant $\frac{1}{2}(C_{11}-C_{12})$ for silver as a function of temperature. The black square marks the room temperature result of Bacon.

Tables I and II show the elastic constants of silver and gold taken from smooth curves drawn to fit the data. In the tables, the 0°K values were obtained by extrapolation of the smooth curves. The number of significant figures is greater than is warranted on an absolute basis but one extra figure has been retained in order to show smoothness and internal consistency. From consideration of the errors, it is estimated that on an absolute basis the directly measured values are accurate to 0.5% and the computed constants to at least 1.5%. The absolute temperature is estimated to be accurate to better than 1.0 degree over the entire range.

In Figs. 1–3 the experimental room-temperature results of Bacon[10] for silver, determined by essentially the same method, are also plotted. Agreement is quite good except in the case of C' where the difference is

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[9] F. C. Nix and D. McNair, Phys. Rev. **61**, 74 (1942).

[10] R. Bacon and Charles S. Smith, Acta Met. **4**, 337 (1956).

about 1%. In Figs. 5–6 the results of Goens[3] for gold are also plotted. The agreement is good for the two shear constants. For the longitudinal mode, $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$, the difference is about $1\frac{1}{2}$% and Goens' value is not plotted since it falls below the graph.

Theoretical Values of the Constants

The low-temperature elastic constants of monovalent metals have been calculated by Fuchs.[6] In his work, the contributions to the constants are considered to come from a sum of terms; W_E, the energy of a positive point lattice in a uniform negative sea; W_V, the Van der Waals energy of a pair of ions; W_I, the ion repulsive energy; W_F, the Fermi energy, and the energy of the lowest state, W_0. Important contributions to the shear constants $C=C_{44}$ and $C'=\frac{1}{2}(C_{11}-C_{12})$ were found to come only from W_I and W_E. Important contributions to the bulk modulus, $B=\frac{1}{3}(C_{11}+2C_{12})$ were found to arise from the ion and Fermi energies. Thus, to this approximation, the elastic constants can be written as a sum of terms:

$$C=C_E+C_I,$$

$$C'=C_E'+C_I',$$

$$B=B_F+B_I,$$

where the subscripts represent the contributions from the ion, electrostatic, and Fermi energies. The electrostatic energy W_E and Fermi energy W_F can be estimated rather simply, but any estimate of the ion energy W_I requires a knowledge of the wave functions of the ion core and then an elaborate calculation. For copper, Fuchs carried out this ion energy calculation using a modified Fermi-Thomas method and obtained elastic constants which are comparable with the low-temperature experimental values.

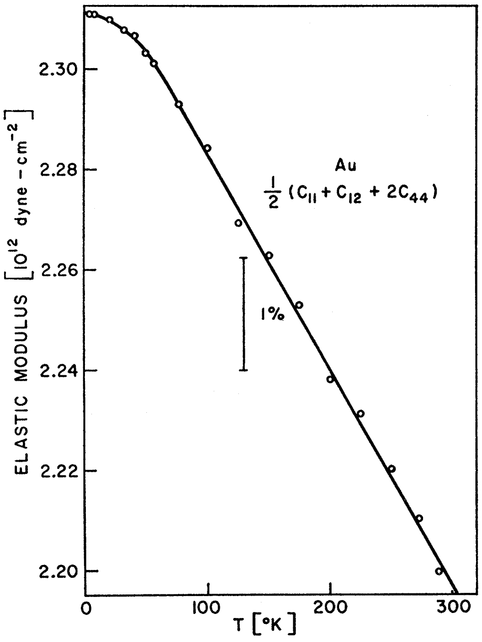

FIG. 4. The adiabatic elastic constant $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ for gold as a function of temperature.

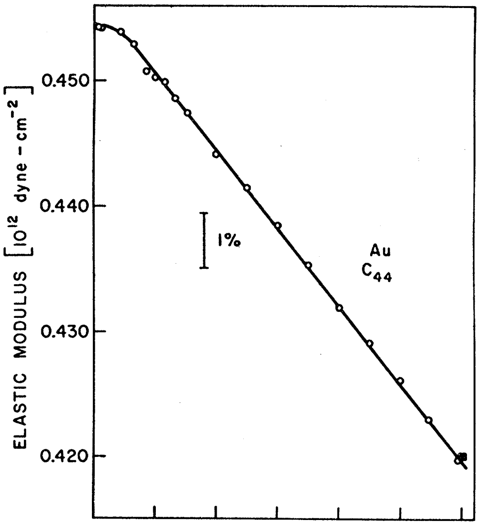

FIG. 5. The adiabatic elastic shear constant C_{44} for gold as a function of temperature. The black square marks the room temperature result of Goens.

Since ion energy estimates are not available for silver and gold, strictly theoretical values of the elastic constants cannot be obtained for these metals. However, by assuming a functional form for the ion energy, the measured elastic constants may be used to determine the parameters in this effective ion-repulsion potential. If only two parameters are introduced, only two elastic constants are needed to specify the ionic term, and the third elastic constant can then be used to judge the validity of the model. Assuming that the effective ion-repulsion potential W_I is given by $W_I=Ae^{(r-r_0)/\rho}$, where r_0 is the distance between ion centers, the two shear constants C and C' were used to determine A

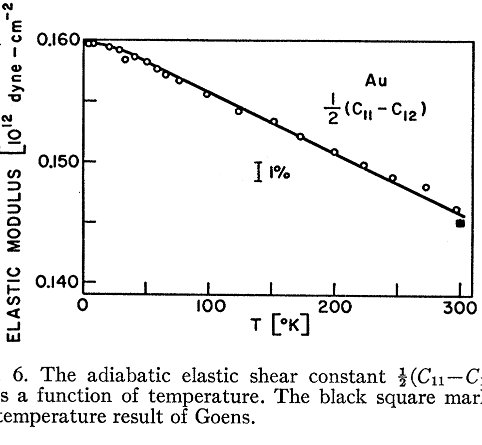

FIG. 6. The adiabatic elastic shear constant $\frac{1}{2}(C_{11}-C_{12})$ for gold as a function of temperature. The black square marks the room temperature result of Goens.

TABLE I. The adiabatic elastic constants of silver as a function of temperature, all in units of 10^{12} dyne cm^{-2}. The first three columns are readings taken from smooth curves drawn through the experimentally determined points. The number of significant figures does not indicate the accuracy of the absolute value (see text).

T (°K)	ρV_1^2 $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$	ρV_2^2 C_{44}	ρV_3^2 $\frac{1}{2}(C_{11}-C_{12})$	C_{11}	C_{12}	B $\frac{1}{3}(C_{11}+2C_{12})$
0	1.6550	0.5109	0.1708	1.3149	0.9733	1.0872
10	1.6545	0.5108	0.1707	1.3144	0.9730	1.0868
25	1.6535	0.5098	0.1704	1.3141	0.9733	1.0869
50	1.6491	0.5072	0.1693	1.3112	0.9726	1.0855
75	1.6407	0.5028	0.1675	1.3054	0.9704	1.0821
100	1.6305	0.4982	0.1657	1.2980	0.9666	1.0771
125	1.6204	0.4936	0.1640	1.2908	0.9628	1.0721
150	1.6103	0.4890	0.1622	1.2835	0.9591	1.0672
175	1.6002	0.4844	0.1604	1.2762	0.9554	1.0623
200	1.5901	0.4797	0.1587	1.2691	0.9517	1.0575
225	1.5800	0.4750	0.1569	1.2619	0.9481	1.0527
250	1.5699	0.4704	0.1551	1.2546	0.9444	1.0478
275	1.5597	0.4658	0.1534	1.2473	0.9405	1.0428
300	1.5495	0.4612	0.1516	1.2399	0.9367	1.0378

and r_0/ρ for silver and gold. Copper was also analyzed in this way for comparison. The results of this calculation are shown on the first two rows of Table III. The third row gives B_I, the contribution to the bulk modulus from the ionic energy as defined from the shear constants. To calculate the total bulk modulus, the bulk modulus B_F of the Fermi gas of electrons in the metal must be added. This was calculated from free electron theory modified for the effective mass of the electrons as determined from specific heat data and is shown in the fourth row of Table III. The fifth row gives the sum (B_F+B_I) which should be the same as the measured total bulk modulus if our semiempirical model is to be a reasonable approximation. Agreement is good for copper, poor for silver, and very bad for gold. Thus at least one of the terms W_E, W_I, or W_F must be a very poor description of gold. The elastic constants are not very sensitive to W_E and since a major modification in it in going from copper to gold would be very difficult to justify, it seems reasonable to assume that W_E is not the main source of the disagreement. The W_I term is presumably adjusted for each of the elements. This leaves only the W_F term and hence the bulk modulus of the electron gas available for modification. DeLaunay[11] has shown that the bulk modulus of the apparent electron gas active in a metal is given by the quantity $C_{12}-C_{44}$. (Actually the difference $C_{12}-C_{44}$ is the bulk modulus arising from all sources whose energies depend upon the total volume rather than on central-force interactions between lattice points.) By taking the measured quantity $C_{12}-C_{44}$ for the bulk modulus of the electron gas and adding it to B_I, the "theoretical" total bulk modulus shown in the seventh row of Table III was obtained. Here the agreement for all three noble metals is greatly improved. The reason that $C_{12}-C_{44}$ is so different from the free-electron bulk modulus B_F in the case of gold is not clear. It may be that the valence electrons cannot be described by the free-electron model used to compute W_F. Also the energy of the lowest state, W_0, may contribute more to the bulk modulus of the heavier noble metals.

Modifying the electronic terms which contribute to the elastic constants is certainly not the only possibility.

TABLE II. The adiabatic elastic constants of gold, in units of 10^{12} dyne cm^{-2}, as a function of absolute temperature. The first three columns are readings taken from smooth curves drawn through the experimentally determined points. The number of significant figures does not indicate the accuracy of the absolute value (see text).

T (°K)	ρV_1^2 $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$	ρV_2^2 C_{44}	ρV_3^3 $\frac{1}{2}(C_{11}-C_{12})$	C_{11}	C_{12}	B $\frac{1}{3}(C_{11}+2C_{12})$
0	2.3109	0.4544	0.1598	2.0163	1.6967	1.8032
10	2.3106	0.4542	0.1597	2.0161	1.6967	1.8032
25	2.3089	0.4533	0.1595	2.0151	1.6961	1.8024
50	2.3032	0.4510	0.1585	2.0107	1.6937	1.7994
75	2.2935	0.4477	0.1572	2.0030	1.6886	1.7934
100	2.2827	0.4446	0.1559	1.9940	1.6822	1.7861
125	2.2721	0.4415	0.1547	1.9853	1.6759	1.7790
150	2.2612	0.4384	0.1535	1.9763	1.6693	1.7716
175	2.2507	0.4352	0.1522	1.9677	1.6633	1.7648
200	2.2397	0.4320	0.1510	1.9587	1.6567	1.7574
225	2.2290	0.4290	0.1497	1.9497	1.6503	1.7501
250	2.2182	0.4257	0.1485	1.9410	1.6440	1.7430
275	2.2076	0.4226	0.1472	1.9322	1.6378	1.7359
300	2.1969	0.4195	0.1460	1.9234	1.6314	1.7287

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[11] J.D eLaunay in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, pp. 219–303.

Reference to Table III shows that the ionic potential parameters are quite different for the different noble metals. This indicates that there may be other contributions to the shear constants or that the electrostatic contributions are too large, as has been suggested by Huntington,[12] or that the simple ionic potential should be modified by introducing noncentral contributions. Following Huntington and using only one-half the contributions from W_E, the ion-potential parameters become somewhat more nearly equal for all three metals and not quite so large, but the failure to describe gold is not improved. The introduction of a noncentral contribution to the ion-ion interaction by assuming $W_I = A'(1+\alpha\phi)e^{(r-r_0)/\rho}$, where α is a constant and ϕ a function of the direction in the lattice (i.e., the second Kubic harmonic), leads to physically unrealistic results. Taking ϕ to be a combination of the second and third Kubic harmonics improves the results but seems to indicate that many harmonics need to be used to obtain consistent values of shear constants and bulk moduli.

TABLE III. Interaction potential parameters and contributions to the bulk modulus for the noble metals. B_I is the ionic contribution to the bulk modulus and B_F the contribution from the Fermi gas of electrons. All the elastic constants are in units of 10^{12} dynes/cm^2.

	Cu	Ag	Au
r_0/ρ	24.2	34.4	80
$W(r_0)$ [ev]	0.016	0.007	0.001
B_I	0.851	0.514	0.407
B_F	0.469	0.356	0.299
B_I+B_F	1.320	0.870	0.706
B_{meas}	1.420	1.087	1.803
$B_I+(C_{12}-C_{44})$	1.283	0.976	1.649
$C_{12}-C_{44}$	0.432	0.462	1.242

Thus it is concluded that if $C_{12}-C_{44}$ is considered to be the bulk modulus of the electron gas, it is possible to arrive at a self-consistent picture of the various contributions to the elastic constants of the noble metals. However, the model is quite empirical and may have no general significance.

Variation With Temperature

It is seen from Figs. 1–6 that the elastic constants of silver and gold are remarkably linear with temperature (deviations being about 0.1%) in the range above 50°K. The temperature variation of both is similar to other metals in that the constants increase with decreasing temperature. However, the variation is different from metals such as copper[4] and zinc[5] in which the curvature is more pronounced. The percentage change of the constants relative to their 0°K values is about the same for silver and gold as for copper. The elastic anisotropy $2C_{44}/(C_{11}-C_{12})$, not shown in the figures, is readily seen from the tables to increase slightly for both metals over the temperature range.

TABLE IV. The intrinsic temperature dependence of the elastic constants of the noble metals [in units of 10^{-4} (deg K)$^{-1}$].

Material		$(\partial \ln M/\partial T)_V$	$(d \ln M/dT)_p$	$\beta K^{-1}(\partial \ln M/\partial p)_T$
Copper	C	−1.64	−3.68	2.04
	C'	−2.64	−4.26	1.62
	B	1.06	−1.60	2.66
Silver	C	−1.15	−4.02	2.87
	C'	−2.26	−4.65	2.39
	B	1.54	−1.88	3.42
Gold	C	−0.01	−2.98	2.97
	C'	−1.31	−3.39	2.08
	B	0.94	−1.66	2.60

The three linear combinations of constants $C=C_{44}$, $C'=\frac{1}{2}(C_{11}-C_{12})$, and $B=\frac{1}{3}(C_{11}+2C_{12})$ completely characterize a cubic crystal. Near room temperature these constants vary linearly with temperature and have the slopes:

$$dC/dT=-1.85,\quad dC'/dT=-0.705,\quad \text{and}\quad dB/dT=-1.95\quad \text{for silver,}$$

$$dC/dT=-1.25,\quad dC'/dT=-0.50,\quad \text{and}\quad dB/dT=-2.87\quad \text{for gold,}$$

all in units of 10^8 dyne cm^{-2} deg^{-1}. All these values were computed from the smoothed curves.

Thinking of the modulus M as an explicit function of temperature, and as an implicit function of temperature through the temperature dependence of the volume, one can write

$$(\partial \ln M/\partial T)_V = (d \ln M/dT)_p + K^{-1}\beta(\partial \ln M/\partial p)_T, \quad (1)$$

where β is the volume expansion coefficient and K is the isothermal compressibility. By evaluation of Eq. (1), it has been shown experimentally[13] that the elastic constants are explicit functions of temperature. Table IV shows Eq. (1) applied to the noble metals, and the values for copper[4] are included for comparison. The values of the isothermal pressure derivatives used in computing the table are taken from Daniels.[14] From Table IV it is clear that the elastic constants of the noble metals are intrinsic functions of temperature. Although for these metals the total change in modulus with pressure is always positive and the total change with temperature is always negative, the intrinsic temperature variation may have either sign. For the shear constants, the intrinsic temperature dependence is negative, and greater for C'. The intrinsic dependence of the bulk modulus is always positive, contrary to results for other metals.[13] On the basis of a simple thermal vibration of the ions, the ionic repulsion would be expected to increase with temperature. The ionic

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[12] H. B. Huntington, Phys. Rev. 91, 1092 (1953).

[13] D. Lazarus, Phys. Rev. 76, 545 (1949); T. R. Long and C. S. Smith, Office of Naval Research Report (unpublished).

[14] W. B. Daniels, dissertation, Case Institute of Technology, 1957 (unpublished).

TABLE V. Debye characteristic temperatures of the noble metals.

Method	Copper	Silver	Gold
Lattice dynamics[a]	345.3	227.4	161.6
Average wave velocity[b]	345.4	227.1	162.2
Calorimetric[c]	343.8±0.5	225.3±0.2	164.6±0.14
Calorimetric[d]	346.7±1.1	226.5±0.5	164.8±0.2
Calorimetric[e]			164.1

[a] See reference 11.
[b] See reference 15.
[c] See reference 16.
[d] See reference 17.
[e] See reference 19.

energy and the Fermi energy, which is not very temperature-sensitive, are the major contributors to the bulk modulus, and it is thus reasonable to expect the intrinsic temperature dependence of the bulk modulus to be positive as is observed here. Since the observed moduli decrease with temperature, one might conclude that both the Fermi energy and the ion repulsion energy are lowered through the increase in volume to more than offset the intrinsic temperature increase.

In the lattice dynamics of DeLaunay,[11] deviations from the Cauchy relations are ascribed to the electron gas which follows the motion of the ions. This deviation, the difference between C_{12} and C_{44}, considered as the bulk modulus of an electron gas, would be expected to decrease with temperature through the thermal expansion. Actually, the difference increases for copper and silver, and decreases for gold. This corroborates DeLaunay's statement that the electron gas as used here is a phenomenological quantity and does not depend on the accuracy of the Sommerfeld theory of the electron gas.

Debye Characteristic Temperatures

In principle, the Debye temperature of a solid may be computed from the low-temperature elastic constants. Various methods are available for carrying out the velocity-averaging over all crystal directions which is necessary for this computation. Betts *et al.*[15] have extended Houston's method to take into account cubic crystals of elastic anistropy greater than 1.5. They find that for anisotropies up to four, taking a six-term approximation gives results which compare with Blackman's numerical integration results to within less than one percent. The case of aluminum is apparently anomalous since the disagreement for such a nearly isotropic metal is large (about 2%).

Using the Born-Von Kármán model of a lattice, modified to include the noncentral electron gas contribution, DeLaunay[11] has also developed a method of calculating Debye temperatures from elastic-constant data. He has shown that using his method for copper, the calculated Debye temperatures are in agreement with calorimetric data to within 0.5%.

Table V compares the Debye temperatures of the noble metals as obtained by various methods. The original calorimetric data of Corak *et al.*[16] are included, as well as a new computation[17] based upon their data but corrected to the 1955 van Dijk and M. Durieux temperature scale.[18] Included also as a matter of interest is a recent unpublished determination[19] of the characteristic temperature of single-crystal gold. This specimen is the remaining part of the ingot from which the acoustic specimen was cut. The elastic and calorimetric determinations of Debye temperature for each metal differ by about 1% for copper and silver and by about 2% in the case of gold. Except for gold, the elastic and calorimetric values of θ_D are very close. The cause of the small discrepancies between the results of the two methods of calculating Debye temperature from elastic constants is probably connected with the approximation methods used in the average velocity method of Betts *et al.* Differences between the calorimetric data are of interest since they represent essentially two different opinions on treatment of the same experimental results. We take Table IV as empirical proof that Debye temperatures derived from elastic and calorimetric measurements are in agreement to within at least 2%. We think the differences are probably not significant and that they indicate the spread in Debye temperature values to be expected. For materials, such as the transition metals, where the calorimetric determination of Debye temperatures is difficult, the calculation of θ_D from low-temperature elastic constants is probably the most accurate method available.

ACKNOWLEDGMENT

The authors wish to thank Mr. E. Runge for making the spectroscopic analysis and Mr. D. Waldorf for his help in preparing the single crystals.

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[15] Betts, Bhatia, and Wyman, Phys. Rev. **104**, 37 (1956).

[16] Corak, Garfunkel, Satterthwaite, and Wexler, Phys. Rev. **98**, 1699 (1955).

[17] J. Skalyo and A. Arrott (to be published).

[18] H. van Dijk and M. Durieux, *Conférence de Physique des Basses Temperatures, Paris,* 1955 (Centre National de la Recherche Scientifique and UNESCO, Paris, 1956).

[19] J. Zimmerman (private communication).