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Anharmonicity in Noble Metals: Some Thermal Properties*

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The room-temperature Grüneisen parameters of copper, silver, and gold have been calculated within the quasiharmonic approximation, using the anisotropic-continuum model and values of the third-order elastic constants recently determined. The agreement between the calculated and the experimental values is good for copper and silver, but only fair (12%) for gold. Expressions for the temperature dependences of the three second-order elastic constants have been derived using the continuum model. These depend upon the second-, third-, and fourth-order elastic constants. The fourth-order elastic constants of copper, silver, and gold have been computed using these expressions, and it was found that they are positive in sign and of the order of 10^{14} dyn/cm^2 in magnitude. Only the closed-shell repulsive interaction between nearest-neighbor ions was taken into account in computing the fourth-order constants. Previous work has indicated that this might be a good approximation for noble metals. The two parameters in the Born-Mayer potential expressing the repulsive interaction were evaluated, and reasonable values were obtained for copper and silver. Anomalous results for gold indicate that contributions to the higher order elastic constants from other than ion-core repulsion cannot be ignored in that metal.

I. INTRODUCTION

SOME of the thermal properties of crystals are directly related to the anharmonic nature of the lattice vibrations. One measure of this anharmonicity is the asymmetry of the lattice potential energy with respect to particle separation. This asymmetry is connected to the higher order elastic constants, namely, the coefficients of the higher order terms in the expansion of the lattice energy in terms of the elastic strain. The third-order elastic constants of the noble metals copper, silver, and gold have recently been determined.[1] (This reference will hereinafter be referred to as I.) It is interesting to calculate some of the thermal properties related to anharmonicity using these values of the third-order elastic constants. The results of such calculations might also be used to evaluate the relative importance of the various contributions to the lattice energy.

The first such thermal property we discuss is the volume thermal expansion β. To calculate β we utilize the quasiharmonic approximation. This means that all thermodynamic and elastic properties of a crystal are assumed to be determined by the harmonic-lattice frequency distribution and its dependence on volume or, more generally, on strain. This dependence is usually specified by defining the scalar-mode Grüneisen parameters

$$\gamma_i = -(V/\nu_i)d\nu_i/dV\,, \tag{1}$$

where V is the volume of the material and ν_i is the frequency of the ith normal mode. In the quasiharmonic approximation ν_i depends only on the state of deformation and is not an explicit function of temperature.[2] Under this assumption, the thermodynamic Grüneisen parameter γ can be defined as a weighted mean of the individual mode parameters, namely,

$$\gamma = \sum_{i=1}^{3N} C_i\gamma_i \Big/ \sum_{i=1}^{3N} C_i\,, \tag{2}$$

where C_i is the specific heat of the ith normal mode. γ is then directly related to the thermal expansion as

$$\gamma = \beta V/K_T C_V\,, \tag{3}$$

where V is the molar volume, K_T is the isothermal compressibility, and C_V the specific heat at constant volume.[3] We see that the calculation of the thermal expansion basically reduces to the calculation of the various γ_i and their weighted mean γ. To perform these calculations we have utilized the anisotropic continuum model. In this case, the γ_i can be calculated if we know the third-order elastic constants.

Sheard[4] evaluated γ in the high- and low-temperature limits from the pressure derivatives of the elastic constants. Collins[5] also used pressure derivatives to calculate the temperature variation of γ for several materials. Their method and results appear to be reasonable. They both used the continuum approximation and took account of finite elasticity theory. Ziman[6] and Foreman[7] proposed another method to calculate the Grüneisen parameter using perturbation theory. Their method is also based on the continuum model, but we consider it to be incomplete because they neglected finite strain considerations which are essential in the continuum treatment. Recently, Brugger[8] derived a new expression for the generalized mode parameters $\gamma_i^{\alpha\beta}$ based upon the general strain dependence of the normal-mode frequencies. He also used the anisotropic

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[1] Yosio Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966).

[2] G. Leibfried and W. Ludwig, Solid State Phys. **12**, 275 (1961).

[3] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), p. 215.

[4] F. W. Sheard, Phil. Mag. **3**, 1381 (1958).

[5] J. G. Collins, Phil. Mag. **8**, 323 (1963).

[6] J. M. Ziman, *Electrons and Phonons* (The Clarendon Press, Oxford, England, 1960), p. 152.

[7] A. J. E. Foreman, Proc. Phys. Soc. (London) **79**, 1124 (1962).

[8] K. Brugger, Phys. Rev. **137**, A1826 (1965).

continuum model, and his treatment takes rigorous account of finite elasticity theory. The formulation requires knowledge of the complete set of third-order elastic constants, for example, six for cubic crystals.

In the present paper, the thermodynamic Grüneisen parameters of copper, silver, and gold were computed using Brugger's formulation for the mode parameters and values of the third-order elastic constants reported in I. It is to be emphasized that the thermal expansion of a cubic crystal is dependent only on the hydrostatic pressure derivatives of the three second-order elastic constants. We have used the Brugger formulation because it is expressed explicitly in terms of the third-order elastic constants. This calculation will, however, only depend upon three linear combinations of the six independent constants for a cubic crystal.

A second thermal property directly related to crystal anharmonicity is the temperature dependences of the elastic constants. Calculation of these quantities should provide a check on the complete set of third-order constants. Expressions for the temperature dependences of the second-order and third-order elastic constants have been derived using the anisotropic continuum approximation. The temperature dependences of the second-order elastic constants are dependent upon the second-, third-, and fourth-order elastic constants of the crystal. Direct calculation of these temperature dependences could not be carried out as there exist no data on the fourth-order constants of any material at the present time. Instead, the fourth-order constants of the noble metals were calculated using experimentally determined values of the temperature dependences of the second-order constants. In order to carry out this calculation, the assumption that only the closed-shell repulsive interaction between nearest-neighbor ions contributes to the fourth-order elastic constants was adopted. This interaction energy was then expressed by a two-parameter Born-Mayer–type potential, and the two parameters were evaluated using the experimental values of the third-order constants and the calculated values of the fourth-order constants. The internal consistency of these calculations and the magnitude of the Born-Mayer parameters so determined provide a check of the assumptions and procedures which we adopted.

II. GRÜNEISEN PARAMETERS

We first summarize Brugger's method of obtaining the generalized mode Grüneisen parameters in terms of the third-order elastic constants. The isothermal generalized-mode Grüneisen parameter is defined by

$$\gamma_i^{\alpha\beta} = -\left[\frac{1}{\nu_i}\left(\frac{\partial \nu_i}{\partial \eta_{\alpha\beta}}\right)_T\right]_{\eta=0}, \tag{4}$$

where $\eta_{\alpha\beta}$ is a component of the Lagrangian strain tensor. This parameter is not intrinsically quasi-harmonic as an explicit temperature dependence is allowed. Adopting the anisotropic continuum approximation and appropriate boundary conditions, Eq. (4) can be written as

$$\gamma_i^{\alpha\beta} = -\frac{1}{2w_i}\left[\frac{\partial(\rho_0 W_i^2)}{\partial \eta_{\alpha\beta}}\right]_{T,\eta=0}, \tag{5}$$

where ρ_0 is the density of the undeformed material, W_i is the wave velocity referred to the unstrained dimension of the crystal, and $w_i = (\rho_0 W_i^2)_{\eta=0}$. By solving the wave equation of small-amplitude waves in a homogeneously deformed medium, Thurston and Brugger[9] derived the expression

$$\rho_0 W_i^2 U_u = [\delta_{uv}\bar{t}_{mn} + (\delta_{vw} + 2\bar{\eta}_{vw})\bar{C}_{munw}{}^S] N_m N_n U_v, \tag{6}$$

where **N** and **U** are the propagation and polarization vectors of the ith normal mode, C^S is a second-order adiabatic elastic constant, and t is the thermodynamic tension $[t_{mn} = \rho_0(\partial U/\partial \eta_{mn})_S = \rho_0(\partial F/\partial \eta_{mn})_T$, where U and F are the internal and free energies per unit mass of the material]. The bar over a symbol indicates that the quantity is to be evaluated in the homogeneously deformed state. By differentiating Eq. (6) with respect to $\eta_{\alpha\beta}$ and evaluating at $\eta=0$, one obtains an expression for the generalized mode Grüneisen parameter:

$$\gamma_i^{\alpha\beta} = -(1/2w_i)[2w_i U_\alpha U_\beta + (C_{\alpha\beta mn}{}^T + C_{\alpha\beta muv}{}^{ST} U_u U_v) N_m N_n], \tag{7}$$

with

$$w_i = C_{muv}{}^S N_m N_n U_u U_v. \tag{8}$$

Summation over repeated indices is always implied. Consecutive superscripts such as ST indicate the nature of the successive derivatives employed to obtain the elastic constant, adiabatic (S) or isothermal (T). For cubic crystals, it can be shown that

$$\gamma_i^T \equiv -\left[\frac{V}{\nu_i}\left(\frac{\partial \nu_i}{\partial V}\right)_T\right]_{P=0} = \tfrac{1}{3}(\gamma_i^{11} + \gamma_i^{22} + \gamma_i^{33}) \tag{9}$$

and the explicit expanded form is expressed as

$$\begin{aligned}\gamma_i^T = -(1/6w)\{&2w + C_{11}{}^T + 2C_{12}{}^T + (C_{111} + 2C_{112})(N_1^2U_1^2 + N_2^2U_2^2 + N_3^2U_3^2)\\ &+ (C_{144} + 2C_{166})[(N_2U_3 + N_3U_2)^2 + (N_3U_1 + N_1U_3)^2 + (N_1U_2 + N_2U_1)^2]\\ &+ 2(C_{123} + 2C_{112})(N_2N_3U_2U_3 + N_3N_1U_3U_1 + N_1N_2U_1U_2)\},\end{aligned}$$

with

$$\begin{aligned}w = C_{11}{}^S(N_1^2U_1^2 + N_2^2U_2^2 + N_3^2U_3^2) &+ C_{44}{}^S[(N_2U_3 + N_3U_2)^2 + (N_3U_1 + N_1U_3)^2 + (N_1U_2 + N_2U_1)^2]\\ &+ 2C_{12}{}^S(N_2N_3U_2U_3 + N_3N_1U_3U_1 + N_1N_2U_1U_2).\end{aligned} \tag{10}$$

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

The components of **N** and **U** refer to the appropriate vectors for the ith normal mode and the elastic constants are expressed in the contracted notation. All third-order constants are of the type ST.

Mode Grüneisen parameters of copper, silver, and gold have been calculated as follows. There exist one longitudinal-like and two transverse-like elastic waves for a given direction **N**. The polarization vectors **U** and, hence, the effective elastic constants w of these waves can be conveniently determined by the method of Quimby and Sutton[10] by solving the elastic wave secular equation. Then γ_i^T can be calculated for any mode using Eq. (10) and values of the second- and third-order elastic constants.

Expressions for the high-temperature and low-temperature limits of the thermodynamic Grüneisen parameter can be obtained from Eq. (2). At high temperatures, $C_i = k$ (the Boltzmann constant) for each of the $3N$ modes, and

$$\gamma_H = \frac{1}{3N} \sum_{i=1}^{3N} \gamma_i^T . \qquad (11)$$

At low temperatures, by assuming the continuum model, it can be shown[4] that

$$\gamma_L = \sum_{i=1}^{3N} \frac{\gamma_i^T}{S_i^3} \Bigg/ \sum_{i=1}^{3N} \frac{1}{S_i^3} , \qquad (12)$$

where S_i is the wave velocity of the ith mode. The Grüneisen parameter at intermediate temperatures is usually calculated by taking account of the variation of C_i with temperature and the assumed frequency distribution.

The γ_H for copper, silver, and gold have been computed from Eqs. (10) and (11) using the room-temperature values of the elastic constants as reported in I. These are summarized in Table I. In computing these quantities it is sufficient to consider propagation directions in a (100)–(110)–(111) triangle on the Debye sphere because of the high symmetry apparent in Eq. (10). A grid over this triangle dividing it into 177 nearly equal areas and having evaluation points at the centers of these areas was constructed. This means that 25 488 modes were considered for each material. All computer calculations were done on the University of Illinois ILLIAC II. Results for γ_H for copper, silver, and gold are presented in Table II together with values determined by experiment.[5] The agreement between the calculated and experimental values is excellent for copper (3.5%), good for silver (6.3%), but only fair for gold (11.7%).

TABLE I. Elastic constants of copper, silver, and gold (in the contracted notation and 10^{12} dyn/cm^2).[a]

	Cu	Ag	Au
c_{11}^S	1.661	1.222	1.929
c_{12}^S	1.199	0.907	1.638
c_{44}^S	0.756	0.454	0.415
C_{111}	−12.71	−8.43	−17.29
C_{112}	−8.14	−5.29	−9.22
C_{123}	−0.50	+1.89	−2.33
C_{144}	−0.03	+0.56	−0.13
C_{166}	−7.80	−6.37	−6.48
C_{456}	−0.95	+0.83	−0.12

[a] Yosio Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966).

TABLE II. Calculated and experimental room-temperature values of the thermodynamic Grüneisen parameter.

	Cu	Ag	Au
γ calc	2.07	2.55	2.65
γ expt[a]	2.0	2.4	3.0

[a] J. G. Collins, Phys. Mag. **8**, 323 (1963).

These discrepancies may originate in the failure of either the quasiharmonic or anisotropic continuum approximations. One example of the over-all success of a harmonic model using the continuum approximation is the Debye theory of specific heat. Some failure of this theory can, however, be seen in the temperature variation of the Debye characteristic temperature Θ. This variation can be satisfactorily explained by adopting a discrete lattice model.[11] The present discrepancy might also possibly be diminished by using a discrete model. Also, the Debye Θ at moderately high temperature determined from specific-heat data and that calculated from elastic data differ. The percent differences are 5.1, 3.6, and 10.8% for copper, silver, and gold, respectively.[11] This may suggest that the continuum or harmonic approximations are not as good in gold as in copper and silver, in agreement with our results.

We also intended to compute the low-temperature limits γ_L, as the continuum model should be a good approximation at low temperatures. However, it was found that values of the Grüneisen parameter calculated by the present method are sensitive to the variation of the third-order constants. For example, $\gamma_L(C_{ij}{}^{0\,°\mathrm{K}}, C_{ijk}{}^{\text{room temp.}} \pm 10\%$ for all $C_{ijk}) = 2.20 \mp 0.60$ for gold. The second-order elastic constants at zero temperature are available.[12,13] Unfortunately, there is no data or even discussion on the temperature variation of the third-order constants of metals. It is possible, though, that the C_{ijk} vary by the indicated amount between room temperature and 0°K. In the case of alkali-halide crystals, Ghate[14] calculated the temperature change of the third-order constants using the Born model of ionic

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[10] S. L. Quimby and P. M. Sutton, Phys. Rev. **91**, 1122 (1953).

[11] M. Blackman, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1955), Vol. 7, Chap. 1, p. 325.

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

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

[14] P. B. Ghate, Phys. Rev. **139**, A1666 (1965).

crystals. His results show, for example, that C_{111} and C_{166} change by -10.8 and -18.4%, respectively, between 300 and 0°K for NaCl. It appears that it may not be meaningful to compute the low-temperature Grüneisen parameters when we have no knowledge of the temperature dependence of the third-order elastic constants. If such knowledge were available, it might tell us something about the temperature dependences of the mode Grüneisen parameters and, hence, the validity of the quasiharmonic approximation.

III. TEMPERATURE VARIATION OF THE ELASTIC CONSTANTS

The Helmholtz free energy of a crystal per unit mass can be written as

$$F=F_0+kT\sum_{i=1}^{3N}\ln\left(2\sinh\frac{\hbar\nu_i}{2kT}\right),\tag{13}$$

where F_0 is the free energy at $T=0$°K in the absence of lattice vibrations. ν_i is the frequency of the ith normal mode and is considered to be a function of the (finite) strain η and the temperature T. Hence, in the following, a quasiharmonic treatment according to which the frequencies would not be explicitly temperature-dependent is not implied. [A detailed discussion of this approach will be given by one of the present authors (AVG) in a separate paper.] By differentiating F twice with respect to strain at constant temperature and using the definition $\gamma_i^{\alpha\beta}=-(1/\nu_i)(\partial\nu_i/\partial\eta_{\alpha\beta})_T$ we obtain

$$\begin{aligned}\left(\frac{\partial^2F}{\partial\eta_{\alpha\beta}\partial\eta_{\gamma\delta}}\right)_T-\left(\frac{\partial^2F_0}{\partial\eta_{\alpha\beta}\partial\eta_{\gamma\delta}}\right)_T &=-\frac{\hbar^2}{4kT}\sum_{i=1}^{3N}\nu_i^2\gamma_i^{\alpha\beta}\gamma_i^{\gamma\delta}\operatorname{csch}^2\frac{\hbar\nu_i}{2kT}\\ &\quad+\frac{\hbar}{2}\sum_{i=1}^{3N}\nu_i\left(\gamma_i^{\alpha\beta}\gamma_i^{\gamma\delta}-\frac{\partial\gamma_i^{\alpha\beta}}{\partial\eta_{\gamma\delta}}\right)\coth\frac{\hbar\nu_i}{2kT}.\end{aligned}\tag{14}$$

Isothermal elastic constants of any order are defined as[15]

$$C_{ijkl}{}^{T}\cdots=\rho_0(\partial^nF/\partial\eta_{ij}\partial\eta_{kl}\cdots)_T,\tag{15}$$

where ρ_0 is the density of the undeformed medium and the elastic constant is expressed in the tensor notation. Using this definition and expanding the hyperbolic functions in terms of $\hbar\nu_i/2kT$, we obtain the relation for the high-temperature limit:

$$C_{\alpha\beta\gamma\delta}{}^{T}(\eta,T)-C_{\alpha\beta\gamma\delta}{}^{0}=-\rho_0kT\sum_{i=1}^{3N}\left(\frac{\partial\gamma_i^{\alpha\beta}}{\partial\eta_{\gamma\delta}}\right)_T.\tag{16}$$

Differentiating Eq. (16) with respect to temperature at constant strain, we have

$$\left(\frac{\partial C_{\alpha\beta\gamma\delta}{}^{T}}{\partial T}\right)_\eta=-k\rho_0\sum_{i=1}^{3N}\left(\frac{\partial\gamma_i^{\alpha\beta}}{\partial\eta_{\gamma\delta}}\right)_T.\tag{17}$$

The term

$$-k\rho_0T\frac{\partial}{\partial T}\left\{\sum_{i=1}^{3N}\left(\frac{\partial\gamma_i^{\alpha\beta}}{\partial\eta_{\gamma\delta}}\right)_T\right\},$$

which is related solely to the deviation from the linear dependence of the elastic constants on temperature, was neglected in this expression. This approximation is supported for Cu, Ag, and Au by the experimentally observed linear behavior at high temperature.[12,13] Further differentiation of Eq. (14) will give, similarly, in the high-temperature limit

$$\left(\frac{\partial C_{\alpha\beta\gamma\delta\rho\sigma}{}^{TT}}{\partial T}\right)_\eta=-k\rho_0\sum_{i=1}^{3N}\left(\frac{\partial\gamma_i^{\alpha\beta}}{\partial\eta_{\gamma\delta}\partial\eta_{\rho\sigma}}\right)_T.\tag{18}$$

It is also easily shown that $\partial C_{\alpha\beta\gamma\delta}{}^{T}/\partial T=0$ and $\partial C_{\alpha\beta\gamma\delta\rho\sigma}{}^{TT}/\partial T=0$ at $T=0$°K.

The quantity $\partial\gamma_i^{\alpha\beta}/\partial\eta_{\gamma\delta}$ can be calculated as follows: Multiplying Eq. (6) on both sides by U_u and differentiating with respect to $\eta_{\alpha\beta}$, we obtain

$$\begin{aligned}\frac{\partial}{\partial\eta_{\alpha\beta}}(\rho_0W_i^2)_T&=-2w_i\gamma_i^{\alpha\beta}(\eta)\\ &=[\bar{C}_{\alpha\beta mn}{}^{T}+2\bar{C}_{mun\alpha}{}^{S}U_uU_\beta\\ &\quad+\bar{C}_{\alpha\beta munv}{}^{ST}U_uU_v\\ &\quad+2\bar{\eta}_{vw}\bar{C}_{\alpha\beta munw}{}^{ST}U_uU_v]N_mN_n.\end{aligned}\tag{19}$$

If Eq. (19) were evaluated at $\eta=0$, we would obtain Eq. (7). We continue to differentiate Eq. (19) with respect to $\eta_{\gamma\delta}$. Evaluating the result at $\eta=0$ gives, after simple but lengthy calculations,

$$\begin{aligned}\partial\gamma_i^{\alpha\beta}/\partial\eta_{\gamma\delta}&=2\gamma_i^{\alpha\beta}\gamma_i^{\gamma\delta}-(1/2w_i)\\ &\quad\times[C_{\alpha\beta\gamma\delta mn}{}^{TT}+4C_{\alpha\beta mun\gamma}{}^{ST}U_uU_\delta\\ &\quad+C_{\alpha\beta\gamma\delta munv}{}^{STT}U_uU_v]N_mN_n.\end{aligned}\tag{20}$$

The fact that Eq. (20) is an $\eta=0$ expression means that the temperature derivatives of Eq. (17) are taken to be those of the zero strain constants. It should be noted that Eq. (20) contains elastic constants of second, third, and fourth order. By further differentiation we could obtain an expression for $\partial^2\gamma_i^{\alpha\beta}/\partial\eta_{\gamma\delta}\partial\eta_{\rho\sigma}$ containing elastic constants up to the fifth order. Substitution of Eq. (20) into Eq. (17) gives an expression for calculating the temperature derivatives of the isothermal second-order elastic constants. The explicit

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

expanded forms for cubic crystals are given as

$$\left(\frac{\partial C_{11}{}^T}{\partial T}\right)_\eta = -k\rho_0 \sum_{i=1}^{3N} \Bigg\{ 2\gamma_i{}^{11}\gamma_i{}^{11} - \frac{1}{2w}\Bigg[C_{111}{}^{TT}N_1{}^2 + C_{112}{}^{TT}(N_2{}^2+N_3{}^2)$$
$$+4C_{111}{}^{ST}N_1{}^2U_1{}^2+4C_{112}{}^{ST}N_1U_1(N_2U_2+N_3U_3)+4C_{166}{}^{ST}[N_1U_1(N_2U_2+N_3U_3)+(N_2{}^2+N_3{}^2)U_1{}^2]$$
$$+C_{1111}N_1{}^2U_1{}^2+2C_{1112}N_1U_1(N_2U_2+N_3U_3)+C_{1122}(N_2{}^2U_2{}^2+N_3{}^2U_3{}^2)+2C_{1123}N_2N_3U_2U_3$$
$$+C_{1144}(N_2U_3+N_3U_2)^2+C_{1155}[(N_1U_3+N_3U_1)^2+(N_1U_2+N_2U_1)^2]\Bigg]\Bigg\}, \quad (21)$$

$$\left(\frac{\partial C_{12}{}^T}{\partial T}\right)_\eta = -k\rho_0 \sum_{i=1}^{3N} \Bigg\{ 2\gamma_i{}^{11}\gamma_i{}^{22} - \frac{1}{2w}\Bigg[C_{112}{}^{TT}(N_1{}^2+N_2{}^2) + C_{123}{}^{TT}N_3{}^2 + 4C_{112}{}^{ST}N_2U_2(N_1U_1+N_2U_2)$$
$$+4C_{123}{}^{ST}N_2N_3U_2U_3+4C_{144}{}^{ST}N_3U_2(N_2U_3+N_3U_2)+4C_{166}{}^{ST}N_1U_2(N_1U_2+N_2U_1)$$
$$+C_{1112}(N_1{}^2U_1{}^2+N_2{}^2U_2{}^2)+2C_{1122}N_1N_2U_1U_2+C_{1123}[N_3{}^2U_3{}^2+2N_3U_3(N_1U_1+N_2U_2)]$$
$$+C_{1255}[(N_2U_3+N_3U_2)^2+(N_1U_3+N_3U_1)^2]+C_{1266}(N_1U_2+N_2U_1)^2\Bigg]\Bigg\}, \quad (22)$$

$$\left(\frac{\partial C_{44}{}^T}{\partial T}\right)_\eta = -k\rho_0 \sum_{i=1}^{3N} \Bigg\{ 2\gamma_i{}^{23}\gamma_i{}^{23} - \frac{1}{2w}\Bigg[C_{144}{}^{TT}N_1{}^2 + C_{166}{}^{TT}(N_2{}^2+N_3{}^2)$$
$$+4C_{144}{}^{ST}N_3N_1U_3U_1+4C_{166}{}^{ST}[(N_2{}^2+N_3{}^2)U_3{}^2+2N_2N_3U_2U_3]+4C_{456}{}^{ST}(N_1U_3+N_3U_1)N_1U_3$$
$$+C_{1144}N_1{}^2U_1{}^2+C_{1155}(N_2{}^2U_2{}^2+N_3{}^2U_3{}^2)+2C_{1255}(N_1N_2U_1U_2+N_1N_3U_1U_3)+2C_{1266}N_2N_3U_2U_3$$
$$+C_{4444}(N_2U_3+N_3U_2)^2+C_{4455}[(N_1U_3+N_3U_1)^2+(N_1U_2+N_2U_1)^2]\Bigg]\Bigg\}, \quad (23)$$

where the elastic constants are written in the contracted notation and all fourth-order constants are of the type STT. The generalized mode Grüneisen parameters can be calculated for cubic crystals from Eq. (7). The expanded forms are

$$\gamma_i{}^{11} = -(1/2w)\{C_{11}{}^TN_1{}^2+C_{12}{}^T(N_2{}^2+N_3{}^2)+2wU_1{}^2+C_{111}N_1{}^2U_1{}^2+C_{144}(N_2U_3+N_3U_2)^2$$
$$+C_{112}[N_2{}^2U_2{}^2+N_3{}^2U_3{}^2+2N_1U_1(N_2U_2+N_3U_3)]$$
$$+2C_{123}N_2N_3U_2U_3+C_{166}[(N_1U_3+N_3U_1)^2+(N_1U_2+N_2U_1)^2]\}, \quad (24)$$

$$\gamma_i{}^{23} = -(1/w)\{C_{44}{}^TN_2N_3+wU_2U_3+C_{144}N_1U_1(N_2U_3+N_3U_2)$$
$$+C_{166}[(N_2{}^2+N_3{}^2)U_2U_3+N_2N_3(U_2{}^2+U_3{}^2)]+C_{456}[N_2N_3U_1{}^2+N_1{}^2U_2U_3+N_1U_1(N_2U_3+N_3U_2)]\}, \quad (25)$$

where all third-order constants are of the type ST. The other elements of the generalized Grüneisen-parameter tensor follow directly by cyclic permutation of the indices.

IV. FOURTH-ORDER ELASTIC CONSTANTS

The temperature coefficients of the second-order isothermal elastic constants can be calculated using the formulation of the preceding section when all second-, third-, and fourth-order elastic constants are known. There are, however, no data available for the fourth-order constants at the present time. Hence, it is interesting to invert the procedure and calculate the fourth-order constants using experimental values of the temperature coefficients.

There are **11** fourth-order elastic constants for cubic crystals.[16,17] Ten of these (all except C_{1456}) appear in the three independent expressions for the temperature derivatives of the second-order constants, $\partial C_{11}{}^T/\partial T$, $\partial C_{12}{}^T/\partial T$, and $\partial C_{44}{}^T/\partial T$. However, in the case of noble metals, simple, approximate relations between the fourth-order constants have been proposed in I:

$$\begin{aligned} &C_{1111}=2C_{1112}=2C_{1122}=2C_{1155}=2C_{1266}=2C_{4444} \\ &C_{1123}=C_{1144}=C_{1255}=C_{1456}=C_{4455}=0. \end{aligned} \quad (26)$$

These relations were obtained by the argument that the contribution from the closed-shell repulsive interaction between nearest-neighbor ions becomes pre-

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[16] T. S. G. Krishnamurty, Acta. Cryst. **16**, 839 (1963).

[17] P. B. Ghate, J. Appl. Phys. **35**, 337 (1964).

TABLE III. Experimental data used in the calculation of fourth-order elastic constants (room-temperature values).

	Cu	Ag	Au
ρ_0 (g/cm^3)	8.96	10.49	19.32
β (10^{-5}/°C)[a]	4.98	5.67	4.26
$(\partial c_{11}{}^T/\partial T)_p$ (10^8 dyn/cm^2 °C)[b]	-5.04	-4.33	-5.53
$(\partial c_{12}{}^T/\partial T)_p$	-3.03	-2.91	-4.52
$(\partial c_{44}{}^T/\partial T)_p$	-2.75	-1.85	-1.25
$B_0{}^T$ (10^{12} dyn/cm^2)[c]	1.313	0.970	1.676
$(\partial c_{11}{}^S/\partial p)_T$ [c]	5.91	5.12	5.72
$(\partial c_{12}{}^S/\partial p)_T$	5.03	3.61	4.96
$(\partial c_{44}{}^S/\partial p)_T$	2.63	3.04	1.52

[a] *International Critical Tables* (McGraw-Hill Book Publishing Company, Inc., New York, 1926), Vol. I, p. 103.
[b] W. C. Overton, Jr., and J. Gaffney, Phys. Rev. **98**, 969 (1955); J. R. Neighbours and G. A. Alers, *ibid.* **111**, 707 (1958).
[c] Yosio Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966).

dominant for determining the higher order elastic constants of materials which have markedly overlapped closed shells. Inserting the relations into our expressions for $\partial C_{ij}{}^T/\partial T$, we can calculate C_{1111}, which is the sole independent fourth-order constant in the present approximation. If our assumptions are justified, the three independent temperature coefficients should yield the same value for C_{1111}.

Computation of C_{1111} was carried out for copper, silver, and gold on ILLIAC II. The lattice sums were approximated by using a 367-point grid over an octant of the Debye sphere. The symmetry apparent in Eqs. (21)–(25) with respect to inversion in the $\{100\}$ and $\{110\}$ coordinate planes indicate that consideration of one octant is sufficient. Room-temperature values of the second- and third-order elastic constants were used (Table I), and the differences between $C_{ijk}{}^{ST}$, the measured third-order constant, and $C_{ijk}{}^{TT}$, which have been shown to be small,[15] were neglected.

It is to be emphasized that only three temperature derivatives of the 81 second-order elastic constant tensor components will give independent, meaningful results. Temperature derivatives of equivalent elastic constants, such as $\partial C_{12}{}^T/\partial T$ and $\partial C_{13}{}^T/\partial T$, will be given by equivalent expressions in terms of higher-order constants. Expressions derived for the temperature derivatives of elastic constants which are identically zero, such as $\partial C_{14}{}^T/\partial T$, appear superficially to give useful information. However, when the lattice sums are handled properly, we see that these expressions are identically zero for any set of elastic constants for a cubic crystal.

In tabulating the temperature derivatives of the elastic constants for computation of C_{1111}, we notice that the quantities calculated in the preceding section are derivatives at constant volume $(\partial C/\partial T)_v$, whereas the usual experimental values are those at constant pressure $(\partial C/\partial T)_p$. These two quantities are related thermodynamically:

$$(\partial C/\partial T)_v = (\partial C/\partial T)_p + B_0\beta(\partial C/\partial p)_T\,, \tag{27}$$

TABLE IV. Calculated values of C_{1111} (in 10^{12} dyn/cm^2).

Computed from	Cu	Ag	Au
$\partial c_{11}{}^T/\partial T$	97.3	83.7	108.5
$\partial c_{12}{}^T/\partial T$	132.8	73.4	120.2
$\partial c_{44}{}^T/\partial T$	73.0	81.8	80.6
Mean	101	80	103

where B_0 is the zero-pressure bulk modulus and β is the volume thermal expansion. These quantities are tabulated in Table III. $(\partial C^T/\partial p)_T$ should be used in Eq. (27), but the differences between $(\partial C^S/\partial p)_T$ and $(\partial C_T/\partial p)_T$ are estimated to be small.

The values of C_{1111} for copper, silver, and gold computed from the three independent second-order elastic constant temperature coefficients are tabulated in Table IV. The consistency between the three values for each material is considered to be sufficient. We believe that the mean values included in Table IV represent reliable estimates of the fourth-order elastic constants C_{1111} of noble metals. This implies that the approximations adopted in this section involving the fourth-order constants should be reasonable. Further considerations involving the lattice energy are discussed in the next section.

V. THE INTERATOMIC POTENTIAL

According to the method of Wigner and Seitz,[18] the energy of a crystal can be expressed as the sum of the ground-state energy of the electrons, the Fermi energy, the electron-electron repulsive energy corrected for exchange and correlation, and the nonelectrostatic energy between ions. The nonelectrostatic interaction between the ion cores in noble metals is usually described by a Born-Mayer energy per ion pair of the form

$$w(r) = A\exp[-B(r/r_0-1)]\,, \tag{28}$$

where r is the separation between ions, and r_0 is the equilibrium separation between nearest neighbors. A and B are material parameters.

It was shown in I that for noble metals the contribution from the repulsive interaction between ion cores becomes more and more predominant in the higher-order elastic constants. If it is assumed that the higher-order elastic constants are determined solely by a repulsive Born-Mayer potential, it has been shown (again in I) that

$$\begin{aligned} C_{111} &= -AB(B^2+3B+3)/2v_0\,,\\ C_{1111} &= AB(B^3+6B^2+15B+15)/4v_0\,, \end{aligned} \tag{29}$$

where v_0 is the volume per atom in the crystal. In ob-

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[18] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); F. Seitz, *ibid.* **47**, 400 (1935).

TABLE V. Born-Mayer parameters calculated from third- and fourth-order elastic constants.

	A (eV)	B
Cu	0.0728	12.67
Ag	0.0374	15.81

taining Eq. (29) only nearest-neighbor interactions were taken into account.

The parameters A and B have been calculated from Eq. (29) using the experimental values of C_{111} (Table I) and the values of C_{1111} determined in the preceding section. The results for copper and silver are presented in Table V. For gold we obtain $B=8.6$ and $A=0.41$ eV. This relatively small value of B for gold appears to contradict the assumption that the repulsive interaction between ion cores is quickly varying. This contradiction will be discussed further below.

Mann and Seeger[19] determined the two Born-Mayer parameters semiempirically for copper, silver, and gold. They adopted four different methods: (a) from the experimental values of the shear moduli and a theoretical expression for the electrostatic shear energy; (b) from the experimental pressure dependences of the shear moduli and a theoretical expression for the electrostatic shear energy; (c) from the experimental values of the bulk modulus and a theoretical expression for the electronic ground-state energy; (d) from the experimental volume-pressure relation and theoretical expressions for several contributions to the crystal energy. Their calculated values of A and B cover a wide range, even within a given method due to undetermined empirical parameters. Method (a) gives the largest range, and includes the highest values of B and lowest values of A. Method (b) covers the smallest range, and includes the lowest values of B and highest values of A. Intermediate results are obtained from methods (c) and (d). Results of methods (a) and (b) are summarized in Table VI.

Numerous other calculations of A and B for copper based on theoretical crystal-energy expressions and input data such as measured elastic constants or phonon dispersion curves have been reported.[20–24] The computed parameters range approximately over the spectrum of values given by Mann and Seeger. Gibson *et al.*[25] calculated defect cascade properties for an irradiated model copper lattice using three sets of Born-Mayer parameters similar to those employed by Huntington.[20] They found that calculated threshold energies to produce a permanently displaced atom were very different for the different parameters. The values $A=0.0510$ eV, $B=13.00$ gave their best values for these energies. The Born-Mayer parameters they used are presented in Table VI.

Thompson[26] studied the scattering of gold ions during channeling experiments. He obtained the values $A=0.11$ eV, $B=14.4$ for this material. This should be a quite basic experiment in the determination of ion-ion interaction parameters. Thompson's results are also included in Table VI.

Our values of the Born-Mayer parameters for copper and silver compare nicely with the values in Table VI. In particular, the agreement with Gibson *et al.* for copper is encouraging. Also, both copper and silver agree well with the "low-B" values of method (a) of Mann and Seeger. The fact that we obtain reasonable Born-Mayer parameters for copper and silver strongly supports the assumptions involved in the calculations of the fourth-order constants of these metals. Specifically, it indicates that contributions to the third-order constants from other than the closed-shell repulsive interaction should be small. As discussed in I, such contributions to the fourth-order constants should be even less. It appears that we have obtained reliable estimates of the fourth-order elastic constants and the Born-Mayer parameters of copper and silver.

The assumptions involved in the calculation of the fourth-order constants require further consideration for gold. Our value of $B=8.6$ for this metal appears low in comparison with even the smallest value reported in Table VI. As mentioned above, a low value of B contradicts the assumption that the repulsive-core interaction varies rapidly enough that it is the only energy term which need be considered. It appears that crystal energies other than the closed-shell repulsive energy contribute significantly to the third-order elastic constants of gold.

This discussion can be made somewhat quantitative. The values of C_{111} measured experimentally $(C_{111})_{\text{meas}}$ are the sum of the closed shell contribution $(C_{111})_c$ and the contribution from all other origins $(C_{111})_e$. We have used $(C_{111})_{\text{meas}}$ in Eq. (29) to calculate B; we should have used $(C_{111})_c$. Equation (29) can be modified to estimate $(C_{111})_e$ and, hence, the error in our calculation of B.

The values of C_{1111} calculated in Sec. IV $(C_{1111})_{\text{calc}}$ can be separated into $(C_{1111})_c$ and $\sum k_{ijkl}(C_{ijkl})_e$, where $k_{ijkl}\ll 1$. The latter can be neglected with respect to $(C_{1111})_c$ if $(C_{111})_e$ is small (though not necessarily negligible) compared with $(C_{111})_c$. This is based on the argument in I that the repulsive core energy should become more predominant as one proceeds to higher-

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[19] E. Mann and A. Seeger, J. Phys. Chem. Solids **12**, 314 (1960).

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

[21] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).

[22] T. Toya, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. 1, p. 25.

[23] H. C. White, Phys. Rev. **112**, 1092 (1958).

[24] S. K. Sinha, Phys. Rev. **143**, 422 (1966).

[25] J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. **120**, 1229 (1960).

[26] M. W. Thompson, Atomic Energy Research Establishment, Harwell, England, Report No. AERE-R-4694, 1964 (unpublished).

TABLE VI. Summary of Born-Mayer parameters obtained by various methods.

	Cu		Ag		Au	
	A (eV)	B	A (eV)	B	A (eV)	B
Mann and Seeger (a)	0.077–0.011	13.6–26.9	0.056–0.008	15.0–32.0	0.040–0.008	16.3–30.5
(b)	0.108–0.075	11.8–12.6	0.088–0.060	12.8–13.8	0.150–0.128	11.6–12.0
Gibson *et al.*	0.0392	16.97				
	0.0510	13.00[a]				
	0.1004	10.34				
Thompson					0.11	14.4

[a] Gave best values for threshold-energy calculations.

order elastic constants. If this is the case, the following relation holds:

$$(C_{111})_e/(C_{111})_{\mathrm{meas}}=1-(C_{1111})_{\mathrm{cal}}/r(C_{111})_{\mathrm{meas}}\,,$$

with

$$r=-(B^3+6B^2+15B+15)/2(B^2+3B+3)\,. \quad (30)$$

Now if we have an estimate of B from some external source, Eq. (30) can be used to calculate the contributions from other than the closed-shell repulsive interaction to the third-order elastic constants. For copper and silver, we believe that other estimates of B are consistent with our own. Hence, such contributions should amount to only a few percent for these metals. For gold, Thompson's value of $B=14.4$ should be quite reliable. Substituting this into Eq. (30) gives $(C_{111})_e/(C_{111})_{\mathrm{meas}}=0.32$. It appears that approximately 30% of the third-order elastic constants of gold originate from other than the closed-shell repulsive interaction.

This fact should not be surprising because we already know that the second-order elastic constants of gold behave differently than those of copper and silver. For example, the Cauchy relation $c_{12}=c_{44}$, which is based on the assumption of central forces, is much further from being satisfied in gold than in copper and silver (see Table I). The ratios c_{12}/c_{44} in copper, silver, and gold are, respectively, 1.59, 2.00, and 3.95, which shows that the contribution of noncentral forces to the elastic properties is more important in gold than in copper and silver. However, we reiterate that the non-closed-shell contribution should become less important as one proceeds to consideration of elastic constants of higher order. This contribution may be far less than 30% for the fourth-order constant of gold, and our calculated value of C_{1111} for that material may be reasonable.

VI. CONCLUSIONS

The thermodynamic Grüneisen parameters of copper, silver, and gold have been computed. In general, the agreement with experiment is good. Slight discrepancies which do exist could be related either to the anisotropic continuum and quasiharmonic approximations adopted in the calculation or to errors in the experimental data.

Expressions for the temperature dependences of the second-order isothermal elastic constants have been derived using the anisotropic continuum model. These expressions have been used to calculate the fourth-order elastic constant C_{1111} of copper, silver, and gold. It was assumed that the fourth-order constants of these metals are related solely to the ion-ion repulsive-core interaction. Despite this simplifying assumption, the results appear surprisingly good for all three metals. Reasonable values of calculated Born-Mayer parameters lend support to this claim for copper and silver. Further work continues to estimate the contribution of the conduction electrons to the higher-order elastic constants. This should improve the results, especially in the case of gold.

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