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Morse-Potential Evaluation of Second- and Third-Order Elastic Constants of Some Cubic Metals

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The second- and third-order elastic constants of Al, Cu, Ag, Au, Na, and K have been calculated in the framework of a central-force model. The interatomic potential was expressed in terms of the Morse potential. The parameters in the potential were determined by using the lattice parameter, bulk modulus, and cohesive energy. The range of the interatomic potential was cut off after 176 and 168 neighbors in the case of face-centered and body-centered cubic metals, respectively. The evaluated second- and third-order elastic constants were used to calculate the pressure derivatives of the second-order elastic constants. These pressure derivatives compare fairly well with the experimental values. The agreement between experimental values and theoretical values of third-order elastic constants is less satisfactory. Theory predicts C_{123} to be positive for all the fcc metals and negative for bcc metals. The available experimental data on the third-order elastic constants of Cu, Ag, and Au show that C_{123} is positive for Ag and negative for Cu and Au. The possible implications of this result are discussed.

INTRODUCTION

EVEN though the interatomic forces in a metal are possibly an admixture of the central, noncentral, and many-body forces, the use of a central-force model in the study of atomic properties is widespread. The main justification for such an approach is that the calculations can be easily handled and the results of such calculations have been rewarding. The Morse potential has been used in the study of second-order elastic constants,[1] equation of state,[1] point defects,[2,3] line defects,[3] etc. The theoretical values obtained by using the Morse potential are in fairly good agreement with the experimental values. In recent years, there has been considerable interest in the study of the third-order elastic constants of metals. These third-order elastic constants are related to the anharmonicity of the solid. It is the purpose of the present article to use the Morse potential to calculate the third-order elastic constants of some of the cubic metals for which experimental data exist. The second-order elastic constants of these metals have also been calculated.

THE MORSE POTENTIAL

Girifalco and Weizer[1] used the Morse potential to calculate the second-order elastic constants for a number of cubic metals. They came to the conclusion that the Morse potential can be used in the study of atomic properties of metals. However, they included the interactions of nearly 1000 neighboring atoms. It is not clear to us whether by including the interactions up to 1000 or so neighboring atoms one could improve the agreement between theory and experiment in spite of the inherent limitations of the central-force model. In order to keep the numerical computations to a fairly manageable size, we have restricted ourselves to 176 and 168 neighboring atoms in the case of face-centered cubic and body-centered cubic metals, respectively. According to the Morse potential, the interaction energy $\phi(r_{ij})$ between the two atoms i and j separated by a distance r_{ij} is given by

$$\phi(r_{ij})=D[e^{-2\alpha(r_{ij}-r_0)}-2e^{-\alpha(r_{ij}-r_0)}]. \qquad (1)$$

The average energy per atom is given by

$$\Phi=\tfrac{1}{2}D\sum_j [e^{-2\alpha(r_j-r_0)}-2e^{-\alpha(r_j-r_0)}], \qquad (2)$$

where r_j is the distance from the origin to the jth atom in the lattice. The summation goes over the 176 and

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[1] L. A. Girifalco and V. G. Weizer, Phys. Rev. **114**, 687 (1959).

[2] P. Hoekstra and D. R. Behrendt, Phys. Rev. **128**, 560 (1962).

[3] R. M. J. Cotterill and M. Doyama, Phys. Rev. **145**, 465 (1966).

TABLE I.[a] Parameters of the Morse potential and data used to evaluate these parameters.

	Lattice parameter[b] Å	Bulk modulus[c] 10^{11} dyn/cm²	Cohesive energy[c] 10^{12} erg/mole	D 10^{-13} erg	α Å^{-1}	r_0 Å
Al	4.050	7.22	−3.22	4.3264	1.0341	3.4068
Cu	3.614	13.09	−3.38	5.2587	1.3123	2.8985
Ag	4.086	10.07	−2.86	5.2118	1.3535	3.1300
Au	4.078	17.32	−3.67	7.6148	1.5830	3.0242
Na	4.290	0.682	−1.09	0.9241	0.5504	5.3678
K	5.32	0.318	−0.91	0.8530	0.4766	6.4130

[a] In a recent article, Cotterill and Doyama (Ref. 3) have reported the values of D, α, and r_0 in the Morse potential used for defect calculations in copper. These authors reported that they included 176 neighbors in their calculations. We used their parameters and repeated the calculations to evaluate the second-order elastic constants as a function of the number of neighboring atoms included. We could reproduce their values of the second-order elastic constants only when 54 neighbors were included. Unfortunately, we have no explanation for this discrepancy.

We have determined the parameters in the Morse potential when 54 and 58 neighboring atoms are included for fcc and bcc metals, respectively. The parameters are, of course, slightly different from the ones reported here. We have calculated the elastic constants using these parameters as well. The over-all agreement between theory and experiment is the same. For lack of space, we report here only the parameters and the values of the elastic constants calculated by including 176 and 168 neighbors on fcc and bcc metals, respectively.

[b] W. B. Pearson, *Handbook of Lattice Spacing and Structure of Metals* (Pergamon Press, Inc., New York, 1958).

[c] Karl A. Gschneidner, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 275.

168 neighboring atoms for fcc and bcc metals, respectively. We have identified Φ as the average cohesive energy per atom. It is convenient to introduce the following quantities:

$$\beta = e^{\alpha r_0}, \tag{3}$$

$$r_j = [m_j^2 + n_j^2 + l_j^2]^{1/2} a = M_j a, \tag{4}$$

where m_j, n_j, and l_j are the position coordinates of any atom in the lattice in terms of half the lattice parameter "a." The atomic volume V_c is $2a^3$ for fcc metals and $4a^3$ for bcc metals. We now impose the equilibrium condition:

$$d\Phi/da = 0 \quad \text{at} \quad a = a_0, \tag{5}$$

so that the lattice is in equilibrium at the observed lattice parameter. The bulk modulus can be expressed as

$$\text{Bulk modulus} = \frac{a_0^2}{9V_c}\left(\frac{d^2\Phi}{da^2}\right)_{a=a_0}. \tag{6}$$

The Morse potential parameters D, α, and r_0 have been determined by using Eqs. (2) to (6) and the experimental values of the lattice parameter, bulk modulus, and cohesive energy. These are listed in Table I.

ELASTIC CONSTANTS

For a cubic crystal, there are three independent second-order elastic constants, namely C_{11}, C_{12}, and C_{44}, and six independent third-order elastic constants (C_{111}, C_{112}, C_{123}, C_{456}, C_{144}, and C_{166}). In this article we use Brugger's[4] definition of the third-order elastic constants.

In the central-force model, the elastic constants obey Cauchy relations:

$$C_{12} = C_{44}, \tag{7}$$

$$C_{112} = C_{166}, \tag{8}$$

$$C_{123} = C_{456} = C_{144}. \tag{9}$$

Hence we have only two and three independent second- and third-order elastic constants. The expressions for the[1] second- and third-order elastic constants are given below when the Morse potential is used:

$$C_{11} = \frac{2D\alpha^2a^2\beta^2}{V_c}\sum_j \frac{m_j^4 e^{-2\alpha a M_j}}{M_j^2} - \frac{D\alpha^2a^2\beta}{V_c}\sum_j \frac{m_j^4 e^{-\alpha a M_j}}{M_j^2} + \frac{D\alpha a\beta^2}{V_c}\sum_j \frac{m_j^4 e^{-2\alpha a M_j}}{M_j^3} - \frac{D\alpha a\beta}{V_c}\sum_j \frac{m_j^4 e^{-\alpha a M_j}}{M_j^3}. \tag{10}$$

The expression for $C_{12}(=C_{44})$ is similar to the one given in Eq. (10) except for the fact that m_j^4 is replaced by $m_j^2 n_j^2$ in all the summations.

$$C_{111} = -\frac{4D\alpha^3a^3\beta^2}{V_c}\sum_j \frac{m_j^6 e^{-2\alpha a M_j}}{M_j^3} - \frac{6D\alpha^2a^2\beta^2}{V_c}\sum_j \frac{m_j^6 e^{-2\alpha a M_j}}{M_j^4} - \frac{3D\alpha a\beta^2}{V_c}\sum_j \frac{m_j^6 e^{-2\alpha a M_j}}{M_j^5} + \frac{D\alpha^3a^3\beta}{V_c}\sum_j \frac{m_j^6 e^{-\alpha a M_j}}{M_j^3} + \frac{3D\alpha^2a^2\beta}{V_c}\sum_j \frac{m_j^6 e^{-\alpha a M_j}}{M_j^4} + \frac{3D\alpha a\beta}{V_c}\sum_j \frac{m_j^6 e^{-\alpha a M_j}}{M_j^5}. \tag{11}$$

The expression for $C_{112}(=C_{166})$ is obtained by replacing m_j^6 by $m_j^4 n_j^2$ in all the summations in Eq. (11). Similarly, the expression for $C_{123}(=C_{456}=C_{144})$ is obtained by replacing m_j^6 by $m_j^2 n_j^2 l_n^2$ in all the summations in Eq. (11).

RESULTS

The second-order elastic constants C_{11} and $C_{12}(=C_{44})$ were calculated for aluminum, copper, silver, gold, sodium, and potassium, using the Morse potential with the parameters listed in Table I. The values of these second-order elastic constants are listed in Table II. The experimental values[5] are also listed in the same table for comparison.

In Table III we list the values of the three third-order elastic (T.O.E.) constants for aluminum, sodium, and potassium. In Table IV we list the values of the T.O.E. constants of copper, silver, and gold. The experimental values of the third-order elastic constants for these metals are also listed in Table IV for comparison.

The hydrostatic pressure derivatives of the second-

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[4] K. Bruggers, Phys. Rev. **133**, A1611 (1964).

[5] See H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 213.

TABLE II. Second-order elastic constants $C_{\alpha\beta}$ in units of 10^{11} dyn/cm^2.

	C_{11} (Theory)	C_{11} (Expt.)	C_{12} (Expt.)	$C_{12}=C_{44}$ (Theory)	C_{44} (Expt.)	Ref.
Al	8.98	10.56	6.39	6.34	2.85	a
		10.82	6.13		2.85	b
Cu	16.36	16.61	11.99	11.46	7.56	c
		16.84	12.14		7.54	d
Ag	12.85	12.22	9.07	8.68	4.54	c
		12.40	9.37		4.61	d
Au	22.75	19.29	16.38	14.60	4.15	c
		19.23	16.31		4.20	d
Na	0.93	0.768	0.645	0.55	0.434	e
		0.738	0.521		0.661	f
K	0.47	0.370	0.314	0.24	0.188	g

[a] D. Lazarus, Phys. Rev. **76**, 545 (1949).
[b] Reference 5.
[c] Reference 7.
[d] Reference 8.
[e] R. H. Martinson, Ph.D. thesis, Cornell University, Ithaca, New York (unpublished).
[f] W. B. Daniels, Phys. Rev. **119**, 1246 (1960).
[g] P. A. Smth and C. S. Smith, J. Phys. Chem. Solids **26**, 279 (1965).

order elastic constants can be easily expressed in terms of the second- and third-order elastic constants,[6]

$$\begin{aligned}\frac{\partial C_{11}'}{\partial p}&=-\frac{2C_{11}+2C_{12}+C_{111}+2C_{112}}{C_{11}+2C_{12}},\\ \frac{\partial C_{12}'}{\partial p}&=-\frac{-C_{11}-C_{12}+C_{123}+2C_{112}}{C_{11}+2C_{12}},\\ \frac{\partial C_{44}'}{\partial p}&=-\frac{C_{11}+2C_{12}+C_{44}+C_{144}+2C_{166}}{C_{11}+2C_{12}}.\end{aligned}\tag{12}$$

$C_{\alpha\beta}'$ are the effective second-order elastic constants that are needed to relate the additional stresses with the infinitesimal strains when the crystal is subjected to hydrostatic pressure. We have used our calculated values of the second- and third-order elastic constants to obtain the values of the pressure derivatives of the second-order elastic constants and also the bulk modulus. These values are listed in Table V.

DISCUSSION

We have used the Morse potential to calculate the second- and third-order elastic constants of aluminum, copper, silver, gold, sodium, and potassium. We have included the interactions up to 176 atoms and 168 atoms in the case of fcc and bcc metals, respectively. We note that the calculated second-order elastic constants (Table II) compare reasonably well with the experimental values. The Cauchy relation $C_{12}=C_{44}$, which is a consequence of the central-force model used, is not satisfied experimentally. The theoretical values of C_{11} are in fairly good agreement with the experimental values of C_{11}. Even though the theoretical values of $C_{12}(=C_{44})$ lie between the experimental values of C_{12} and C_{44}, the theoretical values are generally closer to the experimental values of C_{12} rather than to the experimental values of C_{44}.

TABLE III. Third-order elastic constants $C_{\alpha\beta\gamma}$ in units of 10^{11} dyn/cm^2.

	Al	Na	K
C_{111}	−59.15	−9.28	−4.24
$C_{112}=C_{166}$	−38.55	−1.89	−0.88
$C_{123}=C_{456}=C_{144}$	4.48	−1.97	−1.01

TABLE IV. Third-order elastic constants of Cu, Ag, and Au. Comparison with the experiment[a] ($C_{\alpha\beta\gamma}$ in units of 10^{11} dyn/cm^2).

	Cu	Ag	Au
C_{111} (Theory)	−110.00	−93.22	−184.21
C_{111} (Expt.)	−127.10	−84.3	−172.9
$C_{112}=C_{166}$ (Theory)	−74.88	−62.92	−119.04
C_{112} (Expt.)	−81.4	−52.9	−92.2
C_{166} (Expt.)	−78.00	−63.7	−64.8
$C_{123}=C_{456}=C_{144}$ (Theory)	7.723	4.874	6.141
C_{123} (Expt.)	−5.00	18.9	−23.3
C_{456} (Expt.)	−9.5	8.3	−1.2
C_{144} (Expt.)	−0.3	5.6	−1.3

[a] Reference 7.

We have listed the calculated values of the third-order elastic constants for the metals under study. The T.O.E. constants for copper, silver, and gold are listed separately because the complete set of their T.O.E. constants have been recently determined.[7] The pressure derivatives of the second-order elastic constants are listed in Table V. The experimental values of the pressure derivatives are available for all these metals investigated, and hence a meaningful comparison of the theoretical and experimental values is possible. The theoretical values of C_{111} and C_{112} of Cu, Ag, and Au compare fairly well with the experimental values. However, the Cauchy relation $C_{112}=C_{166}$ is not satisfied by the experimental values. In the case of C_{123}, the agreement between theory and experiment is poor. According to our calculations, C_{123} has a positive sign for fcc metals and a negative sign for bcc metals. For fcc structure, C_{123} is positive because of the intrinsic nature of the potential. In this structure the contributions to C_{123} will start with the third nearest neighbors, the (211) set. We find that only 24 of the nearest 78 atoms contribute to the C_{123} sum. At this distance the first term in the assumed potential has smaller curvature, thus diminishing the magnitude of the negative term of C_{123}. However, in the case of bcc the sum for C_{123} will start with the first nearest neighbors, and includes 64 of the nearest 88 atoms. Hence, the first term in the potential has a substantial effect on C_{123}. The values in Table IV show that C_{123}, C_{456}, and C_{144} have a positive sign for Ag and a negative sign in the case of Cu and

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[6] F. Birch, Phys. Rev. **71**, 809 (1947).

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

TABLE V. Pressure derivatives of the second-order elastic constants. (Experimental values are calculated from room-temperature data.)

	$\frac{\partial C_{11}'}{\partial p}$		$\frac{\partial C_{12}'}{\partial p}$		$\frac{\partial C_{44}'}{\partial p}$		$\frac{\partial B}{\partial p}$		
	Theory	Expt.	Theory	Expt.	Theory	Expt.	Theory	Expt.	Ref.
Al	4.88	7.02	4.06	3.94	2.06	2.20	4.34	4.97	a
		6.24		3.00		2.31		5.19	b
Cu	5.20	5.733	4.32	4.98	2.32	2.63	4.62	5.44	c
		4.66		3.53		2.83		3.91	d
Ag	5.83	4.859	4.73	3.35	2.72	3.04	5.09	4.11	c
		7.03		5.75		2.31		6.18	a
Au	6.69	5.494	5.19	4.73	3.18	1.52	5.68	5.21	c
		7.01		6.13		1.79		6.43	a
Na	4.94	4.03	3.54	3.53	1.54	1.74	4.01	3.70	e
K	4.86	4.31	3.62	3.81	1.63	1.62	4.04	3.97	f

[a] W. B. Daniels and C. S. Smith, *The Physics and Chemistry of High Pressures* (Gordon and Breach, New York, 1963).
[b] R. E. Schmunk and C. S. Smith, J. Phys. Chem. Solids **9**, 100 (1959).
[c] Reference 7.
[d] D. Lazarus, Phys. Rev. **76**, 545 (1949).
[e] R. H. Martinson, Ph.D. thesis, Cornell University, Ithaca, New York (unpublished).
[f] P. A. Smith and C. S. Smith, J. Phys. Chem. Solids **26**, 279 (1965).

Au. The pressure derivatives computed by using the theoretical values of the second- and third-order elastic constants are in reasonable agreement with the experimental values. The quantitative agreement between theory and experiment is within 20 to 25% except in the case of $(\partial C_{44}/\partial p)$ for gold.

Instead of comparing the experimental values of the pressure derivatives with the theoretical values, it may be preferable to compare the combinations of the T.O.E. constants, determined from the experimental values of the pressure derivatives, with the theoretical values. The quantitative agreement between theory and experiment that emerges out of such an approach is similar to the one given in Table IV. It must be mentioned that the disagreement between theory and experiment for C_{123}, even in sign, is somewhat disturbing. It is true that we have neglected the temperature effects in our calculations. However, we believe that the sign of C_{123} for the fcc metals will still be negative even if we fit the parameters in the Morse potential to calculate the elastic constants at 0°K. The room-temperature experimental values of C_{123} for Cu and Au then strongly suggest that the temperature coefficient of C_{123} has a negative sign and is so large in magnitude that the sign of C_{123} changes as the crystals are heated from 0°K to the room temperature. However, we have not calculated the temperature coefficients of the T.O.E. constants of the cubic metals. Experimental data on the temperature variation of the T.O.E. constants of metals are needed.

It is worth mentioning that our calculations are based on a central-force model. In their experimental study of higher-order elastic constants of some noble metals, Hiki and Granato[7] have pointed out the partial success of a central-force model for higher-order elastic constants. The interatomic potential shows an oscillatory behavior as is shown by many authors.[8] In this preliminary study, we have used the Morse potential for our calculations. The over-all quantitative agreement between theory and experiment is satisfactory. The only justification is that the Morse potential gives a physically reasonable description of the atomic properties studied so far. The disturbing result in our calculations is the sign of C_{123} for Cu and Au. We hope that the future experiments will clarify this point.

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[8] W. C. Overton and J. Gaffney, Phys. Rev. **98**, 969 (1955); J. R. Neighbours and G. A. Alers, *ibid.* **111**, 707 (1958).