experimental results of Mackliet[3] who studied tracer diffusion in the analogous system, iron in copper. Mackliet found that while iron diffused in copper with a somewhat higher activation energy than that measured for self-diffusion, the quantitative agreement with theory was extremely poor, and, in fact, the activation energy for iron diffusion was lower than that for the less electropositive impurities, cobalt and nickel. In the present case, the result is in excellent qualitative and quantitative agreement with the screening model, particularly as amplified by the more recent calculations of Blatt[4] and Alfred and March.[5]

TABLE I. Diffusion of ruthenium in silver.

Temperature (°C)	Tracer	Diffusion coefficient (cm²/sec)
945.5	Ru^{103}	$(2.74\pm0.08)\times10^{-10}$
941.7	Ru^{106}	$(2.21\pm0.07)\times10^{-10}$
916	Ru^{106}	$(1.5\ \pm0.2)\ \times10^{-10}$
900.2	Ru^{103}	$(9.6\ \pm0.3)\ \times10^{-11}$
856.2	Ru^{106}	$(3.17\pm0.12)\times10^{-11}$
792.8	Ru^{106}	$(5.5\ \pm0.5)\ \times10^{-12}$

The present result is also qualitatively consistent with the well known rate-theoretic analysis of Wert and Zener,[6,7] although the quantitative agreement is poor. Substituting values of $\beta=0.45$ and $\lambda=0.55$ (which give good results for diffusion of electronegative impurities in silver) into their equation $D_0=a^2\nu\exp(\lambda\beta Q/RT_m)$, and appropriate values for the lattice parameter a, the Debye frequency ν, and the melting temperature T_m, one calculates a value for the frequency factor $D_0=5.9$, considerably less than the measured value.

ACKNOWLEDGMENTS

The original studies of diffusion in the Ru-Ag system were begun in collaboration with C. A. Mackliet and C. T. Tomizuka, and the authors wish to express their sincere thanks for the important contributions made by these individuals. Also, the authors would like to thank J. R. Manning for considerable assistance and advice during the course of the experiment.

---

[3] C. A. Mackliet, Phys. Rev. **109**, 1964 (1958).

[4] F. J. Blatt, Phys. Rev. **99**, 600 (1955).

[5] L. C. R. Alfred and N. H. March, Phys. Rev. **103**, 877 (1956); Phil. Mag. **2**, 985 (1957).

[6] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[7] C. Zener, J. Appl. Phys. **22**, 372 (1951).

PHYSICAL REVIEW VOLUME 114, NUMBER 3 MAY 1, 1959

Application of the Morse Potential Function to Cubic Metals

L. A. GIRIFALCO AND V. G. WEIZER
Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio

(Received December 4, 1958)

The Morse parameters were calculated using experimental values for the energy of vaporization, the lattice constant, and the compressibility. The equation of state and the elastic constants which were computed using the Morse parameters, agreed with experiment for both face-centered and body-centered cubic metals. All stability conditions were also satisfied for both the face-centered and the body-centered metals. This shows that the Morse function can be applied validly to problems involving any type of deformation of the cubic metals.

INTRODUCTION

BECAUSE of the widespread use of central pairwise potential functions in the description of the solid state, a thorough study of the types of problems to which this function may be applied is quite desirable. The purpose of this paper is to investigate the applicability of a special type of pairwise potential function, the Morse function, to the description of the properties of cubic metals.

After discussing the conditions which any potential function must satisfy if it is to describe reality, various crystal properties are expressed in terms of the Morse function. These include the cohesive energy, the lattice constant, the compressibility, the equation of state, and the elastic constants. Calculations are then done to determine the Morse function parameters, which are in turn used to compute the equations of state and the elastic constants for six face-centered and nine body-centered cubic metals.

PROCEDURE

A. General Properties of Potential Functions in Crystals

If $\varphi(r)$ is the energy of interaction of two atoms a distance r apart, then, in order that $\varphi(r)$ represent the interatomic potential of two atoms in a stable crystal, it must satisfy the following conditions:

(1) The force $-\partial\varphi/\partial r$ must be attractive at large r and repulsive at small r; therefore, $\varphi(r)$ must have a minimum at some point $r=r_0$.

(2) The magnitude of φ must decrease more rapidly with r than r^{-3}.

(3) All elastic constants are positive.

(4) $C_{11}-C_{12}>0$, where C_{11} and C_{12} are elastic constants.

Conditions (1) and (2) are results of simple physical considerations. The first arises from the existence of condensed phases, and the second is equivalent to requiring that the cohesive energy be finite. The two conditions taken together guarantee that the crystal will be stable with respect to infinitesimal homogeneous expansions and contractions of the lattice.

Born and his collaborators,[1] through detailed analyses of the stability of crystal lattices, give conditions (3) and (4) for cubic crystal stability. These guarantee that the crystal be stable with respect to infinitesimal shear deformations.

B. Crystal Properties in Terms of the Morse Function

The potential energy $\varphi(r_{ij})$ of two atoms i and j separated by a distance r_{ij} is given in terms of the Morse function by

$$\varphi(r_{ij})=D[e^{-2\alpha(r_{ij}-r_0)}-2e^{-\alpha(r_{ij}-r_0)}], \tag{1}$$

where α and D are constants with dimensions of reciprocal distance and energy, respectively, and r_0 is the equilibrium distance of approach of the two atoms. Since $\varphi(r_0)=-D$, D is the dissociation energy.

In order to obtain the potential energy of a large crystal whose atoms are at rest, it is necessary to sum Eq. (1) over the entire crystal. This is most easily done by choosing one atom in the lattice as an origin, calculating its interaction with all the other atoms in the crystal, and then multiplying by $N/2$, where N is the total number of atoms in the crystal. Thus the total energy Φ is given by

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

where r_j is the distance from the origin to the jth atom. It is convenient to define the following quantities:

$$L=\tfrac{1}{2}ND, \tag{3}$$

$$\beta=e^{\alpha r_0}, \tag{4}$$

$$r_j=[m_j^2+n_j^2+l_j^2]^{\frac{1}{2}}a=M_ja, \tag{5}$$

where m_j, n_j, l_j are position coordinates of any atom in the lattice. Using (3), (4), and (5) in (2), the energy can be written

$$\Phi(a)=L\beta^2\sum_j e^{-2\alpha aM_j}-2L\beta\sum_j e^{-\alpha aM_j}. \tag{6}$$

The first and second derivatives of (6) with respect to a are

$$d\Phi/da=-2\alpha L\beta^2\sum_j M_je^{-2\alpha aM_j}+2L\beta\alpha\sum_j M_je^{-\alpha aM_j}, \tag{7}$$

$$d^2\Phi/da^2=4\alpha^2L\beta^2\sum_j M_j^2e^{-2\alpha aM_j}-2\alpha^2L\beta\sum_j M_j^2e^{-\alpha aM_j}. \tag{8}$$

If, at absolute zero, a_0 is the value of a for which the lattice is in equilibrium, then $\Phi(a_0)$ gives the energy of cohesion, $[d\Phi/da]_{a_0}$ vanishes, and $[d^2\Phi/da^2]_{a_0}$ is related to the compressibility. That is,

$$\Phi(a_0)=U_0(a_0), \tag{9}$$

where $U_0(a_0)$ is the energy of sublimation at zero pressure and temperature,

$$(d\Phi/da)_{a_0}=0, \tag{10}$$

and the compressibility is given by

$$\frac{1}{K_{00}}=V_0\left(\frac{d^2U_0}{dV^2}\right)_{a_0}=V_0\left(\frac{d^2\Phi}{dV^2}\right)_{a_0}, \tag{11}$$

where V_0 = volume at zero temperature, and K_{00} = compressibility at zero temperature and pressure. Using the relation

$$V/N=ca^3,$$

where $c=4$ for body-centered crystals and $c=2$ for face-centered crystals, (11) may be written

$$\frac{1}{K_{00}}=\frac{1}{9cNa_0}\left(\frac{d^2\Phi}{da^2}\right)_{a=a_0}. \tag{12}$$

It is possible to compute the equation of state from Φ. If it is assumed that the thermal part of the free energy can be adequately represented by the Debye model, then the Helmholtz free energy is given by

$$A=\Phi+3NkT\ln(1-e^{-\theta/T})-NkTD(\theta/T), \tag{13}$$

where k = Boltzmann's constant, T = absolute temperature, θ = Debye temperature, and

$$D\left(\frac{\theta}{T}\right)=3\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{x^3}{e^x-1}dx. \tag{14}$$

TABLE I. Morse potential constants for the pairwise atomic interaction in cubic metals, $\varphi=D[e^{-2\alpha(r_j-r_0)}-2e^{-\alpha(r_j-r_0)}]$.

Metal	αa_0	β	L(ev) ×10^{-22}	$\alpha=\text{A}^{-1}$	$r_0=\text{A}$	D(ev)
Pb	2.921	83.02	7.073	1.1836	3.733	0.2348
Ag	2.788	71.17	10.012	1.3690	3.115	0.3323
Ni	2.500	51.78	12.667	1.4199	2.780	0.4205
Cu	2.450	49.11	10.330	1.3588	2.866	0.3429
Al	2.347	44.17	8.144	1.1646	3.253	0.2703
Ca	2.238	39.63	4.888	0.80535	4.569	0.1623
Sr	2.238	39.63	4.557	0.73776	4.988	0.1513
Mo	2.368	88.91	24.197	1.5079	2.976	0.8032
W	2.225	72.19	29.843	1.4116	3.032	0.9906
Cr	2.260	75.92	13.297	1.5721	2.754	0.4414
Fe	1.988	51.97	12.573	1.3885	2.845	0.4174
Ba	1.650	34.12	4.266	0.65698	5.373	0.1416
K	1.293	23.80	1.634	0.49767	6.369	0.05424
Na	1.267	23.28	1.908	0.58993	5.336	0.06334
Cs	1.260	23.14	1.351	0.41569	7.557	0.04485
Rb	1.206	22.15	1.399	0.42981	7.207	0.04644

---

[1] M. Born, Proc. Cambridge Phil. Soc. **36**, 160–172 (1940).

Since the pressure is given by $P=-(\partial A/\partial V)_T$, (13) leads to the equation of state:

$$P=\frac{1}{3ca^2}\frac{d\Phi}{da}+\frac{3\gamma RT}{V}D\left(\frac{\theta}{T}\right), \tag{15}$$

where γ is Grüneisen's constant and V is the volume.

In his first paper on the stability of crystal lattices, Born (reference 1) developed equations by which the elastic constants of cubic monatomic crystals, whose atoms are all at rest and interact according to a central pairwise force law, can be computed from the interatomic potential energy. These equations are

$$C_{11}=\frac{a^4}{2V}\sum_j m_j^4 D_j^2\varphi(r_j), \tag{16}$$

$$C_{12}=C_{44}=\frac{a^4}{2V}\sum_j m_j^2 n_j^2 D_j^2\varphi(r_j), \tag{17}$$

where the operator D_j is defined by

$$D_j=\frac{1}{r_j}\frac{d}{dr_j}, \tag{18}$$

and V is the volume per atom.

Substituting the Morse potential for $\varphi(r_j)$ results in the following:

$$C_{11}=\frac{2D\alpha^2a^2\beta^2}{V}\sum_j\frac{m_j^4e^{-2\alpha aM_j}}{M_j^2}-\frac{D\alpha^2a^2\beta}{V}\sum_j\frac{m_j^4e^{-\alpha aM_j}}{M_j^2}+\frac{D\alpha a\beta^2}{V}\sum_j\frac{m_j^4e^{-2\alpha aM_j}}{M_j^3}-\frac{D\alpha a\beta}{V}\sum_j\frac{m_j^4e^{-\alpha aM_j}}{M_j^3}, \tag{19}$$

$$C_{12}=C_{44}=\frac{2D\alpha^2a^2\beta^2}{V}\sum_j\frac{m_j^2n_j^2e^{-2\alpha aM_j}}{M_j^2}-\frac{D\alpha^2a^2\beta}{V}\sum_j\frac{m_j^2n_j^2e^{-\alpha aM_j}}{M_j^2}+\frac{D\alpha a\beta^2}{V}\sum_j\frac{m_j^2n_j^2e^{-2\alpha aM_j}}{M_j^3}-\frac{D\alpha a\beta}{V}\sum_j\frac{m_j^2n_j^2e^{-\alpha aM_j}}{M_j^3}. \tag{20}$$

C. Numerical Calculations

Calculation of the three constants, α, L, and β, in the Morse potential was performed by solving Eqs. (9), (10), and (11), using experimental values for the energy of sublimation, the compressibility, and the lattice constant. The results are listed in Table I. the experimental values were taken from compilations by Furth[2] and Slater.[3]

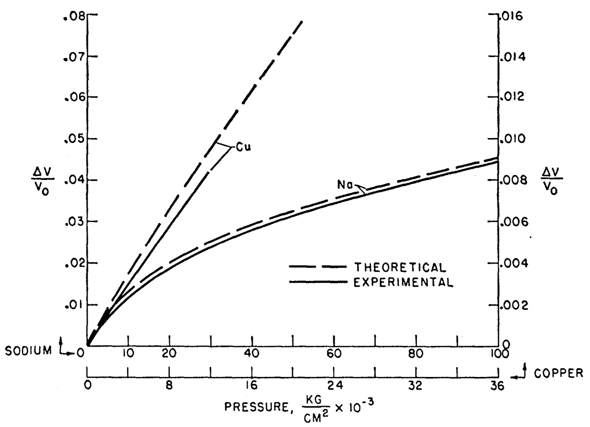

FIG. 1. Equation-of-state curves for copper and sodium.

Equations (15), (19), and (20) permit a straightforward calculation of the equation of state and the elastic constants. Experimental compressibility data, for purposes of comparison, were taken from works by Bridgman[4]; values of θ and $D(\theta/T)$ were taken from existing tables.[5–9] In order to compensate for errors in the selection of θ, and to give a consistent set of values of γ, γ was obtained by calculating it from the requirement that at one atmosphere pressure, Eq. (15) must lead to the correct molar volume. The values of γ computed in this way are given in Table II.

All lattice summations were calculated using an IBM-653 digital computer.

RESULTS AND CONCLUSIONS

In applying the four stability criteria to the Morse potential function, the following results are found:

1. Condition (1) is satisfied. This is obvious from inspection of Eq. (1).
2. Condition (2) is satisfied. This stems from the fact that finite values of the Morse parameters are obtained when a finite value of the energy of vaporization is assumed. A list of the calculated parameters is given in Table I.
3. Condition (3) is satisfied. All the calculated elastic constants are positive as can be seen from Table II. Also contained in Table II are the experimental values

---

[2] R. Furth, Proc. Roy. Soc. (London) **A183**, 87–110 (1944).

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

[4] P. Bridgman, Proc. Am. Acad. Arts Sci. **58**, 151–161 (1923); **60**, 385–421 (1925); **60**, 305–383 (1925); **67**, 345–375 (1932); **74**, 11–20 (1940); **74**, 21–51 (1940); **74**, 425–440 (1942).

[5] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939).

[6] N. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford University Press, London, 1936).

[7] C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1953).

[8] W. P. Binnie, Phys. Rev. **103**, 579–80 (1956).

[9] E. J. Post, Can. J. Phys. **31**, 112–119 (1953).

TABLE II. Values of Grüneisen's constant γ and the elastic constants.

Metal	$C_{11}\times10^{-12}$ (theory)	$C_{11}\times10^{-12}$ (expt.)	$C_{12}\times10^{-12}$ (theory)	$C_{12}\times10^{-12}$ (expt.)	$C_{44}\times10^{-12}$ (expt.)	γ
Pb	0.5565	0.67 (0°K)	0.3705	0.57 (0°K)	0.189 (0°K)	0.951
Ag	1.3239	1.240	0.8959	0.934	0.461	2.287
Ni	2.3292	2.50	1.6348	1.60	1.185	3.252
Cu	1.7424	1.762 (0°K)	1.2309	1.249 (0°K)	0.818 (0°K)	2.108
Al	0.9396	1.129	0.6721	0.665	0.278	1.000
Ca	0.2079		0.1509			0.925
Mo	2.9408	4.6	2.8944	1.79	1.09	0.0
W	3.3828	5.01	3.2773	1.98	1.514	0.0
Cr	2.0128		1.9625			0.0
Fe	1.8586	2.37	1.6735	1.41	1.160	0.164
Ba	0.10579		0.0919			1.497
K	0.0345	0.0459 (77°K)	0.0282	0.0372 (77°K)	0.0263 (77°K)	1.932
Na	0.0712	0.0945 (90°K)	0.0578	0.0779 (90°K)	0.0618 (0°K)	1.216
Cs	0.01800		0.0146			0.619
Rb	0.0233		0.0187			0.635

of the elastic constants.[10] The experimental and theoretical values of C_{11} are in reasonable agreement. The theoretical values of C_{12} are generally in closer agreement with the experimental C_{12} values than the experimental C_{44} values. The Cauchy relation $C_{12}=C_{44}$, which is a consequence of any central force law, is of course not satisfied experimentally in metals.

4. Condition (4) is satisfied.

It is also found that the theoretical equations of state compare quite favorably with experiment. Figure 1 gives a typical comparison between the theoretical and experimental equation of state curves. Equation-of-state calculations for the other metals show about the same degree of agreement between theory and experiment.

It can be concluded, therefore, that for cubic metals, the Morse potential can be applied to problems involving any kind of a lattice deformation, that is, either homogeneous expansion or contraction, or shear deformation.

The estimates of the validity of the Morse potential in metals given in the preceding paragraphs apply to a perfect crystal. An additional complication is introduced if defects are present. The Morse constants computed from the energy of vaporization, the lattice constant, and the compressibility refer to a perfect lattice, and reflect its electron distribution. The presence of a defect, however, alters the electron distribution, and it is difficult to estimate how this altered distribution would affect the Morse constants of the atoms in the vicinity of the defect. It would be expected, however, that this effect would be more serious for body-centered than for face-centered materials.

For a more detailed treatment of the calculations mentioned in this paper, the reader is referred to an NASA report No. 5, 1958, by L. A. Girifalco and V. G. Weizer.

---

[10] J. deLaunay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.