tions of $F_2^+$ centers.

$F_2$ centers become ionizable, and their optical-absorption band is measurable when the electron ejected from an $F_2$ center becomes permanently trapped. The electron trap is a halogen ($V$) center core which forms an excess electron center called here the $\psi$ center.

$F_3$ centers were also ionized by the so-called $M_L$ light.[12] It is reasonable, therefore, to assume that there are $R_L$ bands associated with $F_3$ centers just as there are $M_L$ bands associated with $F_2$ centers.[12]

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†Preliminary results were presented at the Philadelphia, March 1969, American Physical Society Meeting.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 2 15 JULY 1970

# Mechanical Stability of Crystal Lattices with Two-Body Interactions

Frederick Milstein*

*University of California, Santa Barbara, California* 93106

(Received 17 March 1970)

The stability criteria developed by Max Born are applied to investigate the mechanical stability of body-centered-cubic (bcc) and face-centered-cubic (fcc) Morse-function crystal lattices {i.e., lattices in which the atoms interact via the morse interatomic potential energy function $\varphi(r) = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}]$}. It is shown that the conditions for stability can be expressed uniquely as a function of $\alpha a$, where $a$ is the lattice parameter of the crystal. The fcc lattice is stable for all values of $\alpha a$, while the bcc lattice is stable only for values of $\alpha a$ which are less than 4.8. The possibility of using Morse-function lattices to represent cubic crystals with particular values of elastic moduli $C_{11}$ and $C_{12}$ is investigated. The Morse function can serve quite well for this type of representation for fcc crystals. For bcc crystals, however, the ratio $C_{11}/C_{12}$ does not exceed about 1.36; thus the representation is inherently fairly poor.

## INTRODUCTION

Max Born[1] investigated the conditions under which a crystal lattice will be thermodynamically stable. Necessary conditions for the thermodynamic stability of a crystal lattice are that the crystal be mechanically stable with respect to arbitrary (small) homogeneous deformations. Born[1] derived mathematical expressions for these stability requirements (referred to as the Born stability criteria) for cubic lattices of the Bravais type on the assumption of central forces of a very general type.

In the present paper, the stability of cubic crystal lattices, in which the atoms interact via the two-body Morse[2] interatomic potential function, is investigated in terms of the Born criteria. This study was prompted by the fact that empirical two-body interatomic potential functions such as the Morse or the inverse power functions are often used for representing interatomic interactions in investigations of a wide variety of phenomena. For example, these functions have been applied to studies[3] of elastic moduli of metals[4, 5] and alloys,[6] lattice distortion at surfaces,[7, 8] shock wave propagation in cubic crystals,[9] equations of state,[4,10] and the defect structure of solids, including point defects[11,12] and dislocations.[13,14]

A factor which bears upon the general applicability of a particular two-body interatomic potential function in studies such as those indicated above[15] is whether or not the crystal lattice (considered to be made up of pairwise interacting atoms) is inherently stable. Thus the question of whether or not such crystal lattices are stable, in terms of the Born stability criteria, is of both practical and theoretical interest.

For two-body central forces, Born[1] suggested that the face-centered-cubic (fcc) crystal lattice is completely stable, the body-centered-cubic (bcc) lattice is only stable under certain conditions (long-range shallow interatomic potentials), and the simple-cubic (sc) lattice is always unstable. Misra[16] investigated numerically the stability of cubic lattices with a particular form of interatomic interaction, viz., the inverse power or Mie[17] potential $\varphi(r) = -ar^{-m} + br^{-n}$ $(n > m)$. He found that a fcc crystal lattice always satisfies the Born stability criteria, a bcc lattice only satisfies the Born criteria for values of $n < 5$ (hence the lattice is mechanically unstable if $n$ is larger than 5), and the sc lattice is always unstable. These results have been of interest to studies concerned with applying the Mie potential function to calculate particular properties or behavior of cubic crystals.[9-11]

In recent years, applications of the Morse interatomic potential function have become increasingly widespread in the description of the solid state.[4-9,12,13] Thus it is also of interest to study the mechanical stability, in terms of the Born criteria, of cubic crystal lattices in which the atoms interact through the Morse interatomic potential function (such a crystal lattice is referred to, herein, as a Morse-function lattice).

Girifalco and Weizer[4] studied the applicability of the Morse function to the description of cubic metals. In their study, the requirement that the Morse-function lattice be stable, in terms of the Born criteria, was a principal condition for the applicability of this potential function. They found that for each case (which includes six fcc and nine bcc metals) that they investigated, the Morse-function crystal lattice satisfied the Born criteria. Thus they concluded "that for cubic metals, the Morse potential can be applied to problems involving any kind of lattice deformation, that is, either homogeneous expansion or contraction, or shear deformation."

The following questions are stimulated by the results of Girifalco and Weizer's study: (a) Does a Morse potential always result in stable[18] fcc and bcc lattices? (b) If the answer to the above question is negative, what are the conditions under which the Morse-function crystal satisfies the Born criteria? In particular, can the requirements for the stability of the Morse-function lattice be expressed in simple terms? That is, can results be obtained which are analogous to those of Misra in which the fcc lattice is always stable and the bcc lattice is unstable for values of the repulsive exponent $n > 5$ (for two-body interactions of the form $-ar^{-m} + br^{n}$)?

In addition, the Morse potential has been applied to the calculation of first-order[4] and higher-order[5] elastic constants of cubic crystals. Thus, one is led to ask (c) are there restrictions upon the values of elastic constants which Morse-function cubic crystals may possess (i.e., restrictions other than those resulting directly from the condition of central forces, such as $C_{12} = C_{44}$)? In other words, can the Morse-function cubic crystal have arbitrary values of $C_{11}$ and $C_{12}$, or are the values constrained to lie within certain natural limits?

The present paper answers the above questions (a)-(c).

## THEORY

### A. Born Stability Criteria

The Born stability criteria are discussed in detail in Chap. III (on elasticity and stability) of Born and Huang.[19] Briefly, in order for a simple crystal lattice to be mechanically stable, the quadratic form representing the strain energy function,

$$\tfrac{1}{2}\sum_{i,j} C_{ij}\, S_i\, S_j \;,$$

must be positive definite so that any combination of small strains $S_i$ will result in an increase in energy. The $C_{ij}$ are the elastic constants.

According to an algebraic theorem,[20] the above quadratic form is positive definite if the determinants of the matrices of successive orders (the principal minors), as marked out in the following matrix, are all positive:

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix}$$

For crystals of cubic symmetry, there are only three independent elastic constants, say, $C_{11}$, $C_{12}$, and $C_{44}$; in addition, for central forces, the Cauchy relations yield $C_{12} = C_{44}$, so that the above matrix of quadratic coefficients reduces to

$$\begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{12} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{12} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{12} \end{pmatrix} .$$

The principal minors of this matrix are $C_{12}$, $C_{12}^2$, $C_{12}^3$, $C_{12}^3 C_{11}$, $C_{12}^3 (C_{11}^2 - C_{12}^2)$, and $C_{12}^3 (C_{11} - C_{12})^2 (C_{11} + 2C_{12})$. The conditions for all of these terms to be positive can be expressed simply as

$$C_{12} > 0, \tag{1}$$

$$\text{and} \quad C_{11} > C_{12} \quad \text{or} \quad C_{11}/C_{12} > 1 . \tag{2}$$

In order to relate the stability of cubic lattices to the nature of the interatomic force law for the idealized case of pairwise interatomic interactions, Born[1] developed formulas which express $C_{11}$ and $C_{12}$ in terms of the interatomic potential $\varphi(r)$. These formulas may be written as

$$C_{11} = \frac{na}{8} \sum_{l_1} \sum_{l_2} \sum_{l_3} l_1^4 \psi''(r) \tag{3}$$

$$\text{and} \quad C_{12} = \frac{na}{8} \sum_{l_1} \sum_{l_2} \sum_{l_3} l_1^2 l_2^2 \psi''(r) \ , \tag{4}$$

$$\text{where} \quad r = (a/2)(l_1^2 + l_2^2 + l_3^2)^{1/2} \tag{5}$$

$$\text{and} \quad \psi'' = \frac{d^2\varphi}{(dr^2)^2} . \tag{6}$$

$n$ is the number of atoms per unit cell (4 for fcc and 2 for bcc), the lattice parameter $a$ is the length of a cube edge of the unit cell, and $r$ is the distance from a lattice site, chosen as the origin, to a given lattice site with coordinates specified by three integers $l_1$, $l_2$, and $l_3$. The summations in Eqs. (3) and (4) are over all[21] lattice sites (except for the origin $l_1 = l_2 = l_3 = 0$) in the crystal; these summations are accomplished by summing over integer values of $l_1$, $l_2$, and $l_3$ subject to the restrictions that $l_1 + l_2 + l_3$ is an even integer for a fcc lattice, and $l_1$, $l_2$, and $l_3$ are either all even or all odd for a bcc lattice. $\varphi$ is of course the pairwise potential energy for two atoms as a function of their mutual separation $r$. It is noted that although the atoms interact through a "two-body" potential function $\varphi$, each atom interacts with all of the other atoms in the crystal; the contributions of these interactions are taken into account by summing over all[21] of the lattice sites in the expressions for $C_{11}$ and $C_{12}$.

For a given two-body interaction $\varphi$, the lattice parameter $a$ (i.e., the equilibrium value of $a$) is determined by the condition of equilibrium of forces for the crystal, viz.,

$$\sum_{l_1} \sum_{l_2} \sum_{l_3} l_1^2 \psi'(r) = 0 \ , \tag{7}$$

$$\text{where} \quad \psi' = \frac{d\varphi}{dr^2} . \tag{8}$$

Thus, for a cubic crystal consisting of atoms or ions which interact via a two-body interatomic potential function $\varphi(r)$, the condition for equilibrium of the lattice is that the lattice sum of Eq. (7) be equal to zero; the conditions for a *stable equilibrium* (with respect to small homogeneous deformations) are that the lattice sum of Eq. (4) be positive and the lattice sum of Eq. (3) be greater than that of Eq. (4), i.e., $C_{11} > C_{12} > 0$. These conditions express the Born stability criteria for a cubic crystal with two-body central force interactions.

Misra[16] studied the stability of the general inverse power potential cubic lattice in terms of these conditions, and Girifalco and Weizer[4] applied these criteria to study the stability of some specific Morse-function fcc and bcc lattices. The present paper applies the Born criteria to investigate the stability of the general Morse-function fcc and bcc lattice.

### B. Morse Interatomic Potential Function

The Morse function expresses the potential energy $\varphi(r)$ between two atoms separated by a distance $r$ as

$$\varphi(r) = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}] \ , \tag{9}$$

where $D$ and $\alpha$ are constants with dimensions of energy and (distance)$^{-1}$, respectively. The potential has its minimum at $r = r_0$, and the dissociation energy of the two atoms is $D$, since $\varphi(r_0) = -D$.

For brevity of notation, let

$$P = De^{2\alpha r_0} \tag{10}$$

$$\text{and} \quad Q = 2De^{\alpha r_0} \quad . \tag{11}$$

Then, for the Morse function, Eqs. (8) and (6) yield

$$\psi'(r) = -(P\alpha/r)e^{-2\alpha r} + (Q\alpha/2r)e^{-\alpha r} \tag{12}$$

$$\text{and} \quad \psi''(r) = P\left[\frac{\alpha^2}{r^2} + \frac{\alpha}{2r^3}\right]e^{-2\alpha r} - Q\left[\frac{\alpha^2}{4r^2} + \frac{\alpha}{4r^3}\right]e^{-\alpha r} \ . \tag{13}$$

In the following section, expressions (12) and (13) are used together with Eqs. (3), (4), and (7) to investigate the stability of the general Morse-function fcc and bcc lattice. It is shown that the

Born stability criteria can be expressed uniquely as a function of the dimensionless parameter $\alpha a$. Explicit numerical results are obtained and are compared with the results of others, where appropriate.

## CALCULATION OF LATTICE STABILITY

In order to perform the lattice summations indicated in the previous section, and to demonstrate that the stability criteria can be expressed uniquely in terms of $\alpha a$, it is convenient to define the dimensionless variable

$$\rho = r/a = \tfrac{1}{2}(l_1^2 + l_2^2 + l_3^2)^{1/2} \ , \tag{14}$$

and to express Eqs. (12) and (13), respectively, as

$$\psi'(r) = -\frac{P}{2a^2}\left[\frac{2\alpha a}{\rho}\, e^{-2\alpha a\rho}\right] + \frac{Q}{2a^2}\left[\frac{\alpha a}{\rho} e^{-\alpha a\rho}\right]$$

$$= -\frac{P}{2a^2} f(l_1, l_2, l_3;\, 2\alpha a) + \frac{Q}{2a^2} f(l_1, l_2, l_3; \alpha a) \tag{15}$$

and

$$\psi''(r) = \frac{P}{4a^4}\left[\left(\frac{2\alpha a}{\rho}\right)^2 - \frac{2\alpha a}{\rho^3}\right] e^{-2\alpha a\rho}$$

$$- (Q/4a^4)\,[(\alpha a/\rho)^2 + \alpha a/\rho^3]\, e^{-\alpha a\rho}$$

$$= \frac{P}{4a^4} g(l_1, l_2, l_3;\, 2\alpha a) - \frac{Q}{4a^4} g(l_1, l_2, l_3;\, \alpha a). \tag{16}$$

The meaning of the functions $f$ and $g$ is clear from usage.

Equations (15) and (16) may be substituted into Eqs. (3), (4), and (7), and the lattice summations may be performed over the allowed values of the integers $l_1$, $l_2$, and $l_3$. The following lattice summations are functions only of $\alpha a$ and of the particular lattice type, i.e., fcc or bcc:

$$\sum_{l_1}\sum_{l_2}\sum_{l_3} l_1^2 f(l_1, l_2, l_3; \alpha a) = F(\alpha\alpha) \ , \tag{17}$$

$$\sum_{l_1}\sum_{l_2}\sum_{l_3} l_1^4 g(l_1, l_2, l_3; \alpha a) = G(\alpha a) \ , \tag{18}$$

$$\sum_{l_1}\sum_{l_2}\sum_{l_3} l_1^2 l_2^2 g(l_1, l_2, l_3; \alpha a) = H(\alpha a) \ . \tag{19}$$

The equilibrium condition, Eq. (7), may now be expressed as

$$P F(2\alpha a) = Q F(\alpha a) \tag{20}$$

and the elastic constants may be written as

$$C_{11} = (n/32a^3)[P G(2\alpha a) - Q G(\alpha a)] \tag{21}$$

$$\text{and } C_{12} = (n/32a^3)[P H(2\alpha a) - Q H(\alpha a)] \ . \tag{22}$$

The equilibrium condition, Eq. (20), is satisfied if the coefficients $P$ and $Q$ are in the proper ratio; Eq. (20) shows that this ratio is determined uniquely by the value of the parameter $\alpha a$. If Eq. (20) is substituted into Eq. (22), $C_{12}$ may be written as

$$C_{12} = \frac{nP}{32a^3}\left[G(2\alpha a) - \frac{F(2\alpha a)}{F(\alpha a)} G(\alpha a)\right] \ . \tag{23}$$

Since $nP/32a^3$ is positive for the Morse function, the first stability condition $C_{12} > 0$ is satisfied if the function in the brackets in Eq. (23) is positive. In the present study, this function was evaluated for bcc and fcc lattices for values of $\alpha a$ from 0.5 to 20.0, and was found to be positive throughout.

Thus the question of whether a bcc or fcc Morse-function lattice satisfies the Born stability criteria is reduced to the question of whether relation (2), $C_{11}/C_{12} > 1$, is satisfied. This relation can be expressed uniquely as a function of $\alpha a$, viz.,

$$\frac{C_{11}}{C_{12}} = \frac{G(2\alpha a) - [F(2\alpha a)/F(\alpha a)]G(\alpha\alpha)}{H(2\alpha a) - [F(2\alpha a)/F(\alpha a)]H(\alpha a)} > 1. \tag{24}$$

The above expression for $C_{11}/C_{12}$ results from combining Eqs. (20), (21), and (23).

From the above discussion, it is seen that the conditions for the stability of the Morse-function cubic lattice with respect to homogeneous deformations may be expressed uniquely as a function of the dimensionless parameter $\alpha a$. The appropriate lattice summations were evaluated upon an electronic computer for bcc and fcc lattices, and the ratio $C_{11}/C_{12}$ was determined as a function of $\alpha a$. The results of these calculations are presented in the following section.

## RESULTS AND DISCUSSION

Since the Born stability criteria for the Morse-function cubic lattice can be expressed as the condition $C_{11}/C_{12} > 1$, and since the ratio $C_{11}/C_{12}$ depends only upon $\alpha a$ and the type of lattice, it is convenient to present the results of the present calculations as curves of $C_{11}/C_{12}$ versus $\alpha a$ for the fcc and the bcc lattices. These curves are shown in Figs. 1 and 2, respectively, for fcc and bcc lattices.

Figure 1 shows that $C_{11}/C_{12}$ is evidently greater than unity for all values of $\alpha a$ for the fcc lattice. Thus the fcc Morse-function lattice always satisfies the Born criteria. For the bcc lattice, however, $C_{11}/C_{12}$ is less than unity for values of $\alpha a$ greater than 4.8; thus the bcc Morse-function lattice is unstable for $\alpha a$ greater than 4.8. From the discussion in Born and Huang[19] (pp. 140–144), one concludes that the bcc lattice will be stable only when the distance $(r_I - r_0)$ is relatively large; $(r_I - r_0)$ is the distance between the inflection point at $r = r_I$ and the minimum at $r = r_0$ of the potential curve $\varphi(r)$. For the Morse potential function,

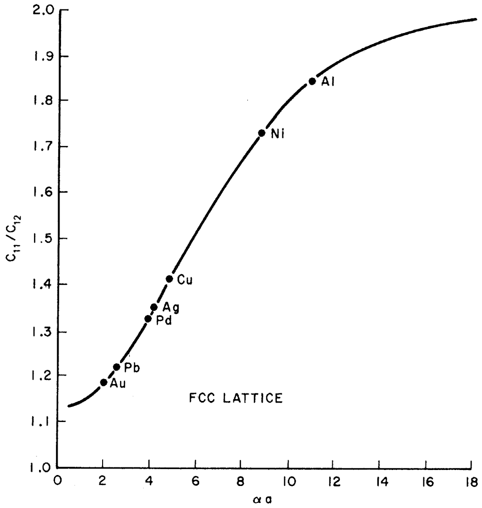

FIG. 1. Ratio of elastic constants $C_{11}/C_{12}$ versus $\alpha a$ for Morse-function fcc lattices. Experimental values of $C_{11}/C_{12}$ are indicated for seven fcc metals. The Born stability criteria are satisfied for all values of $\alpha a$.

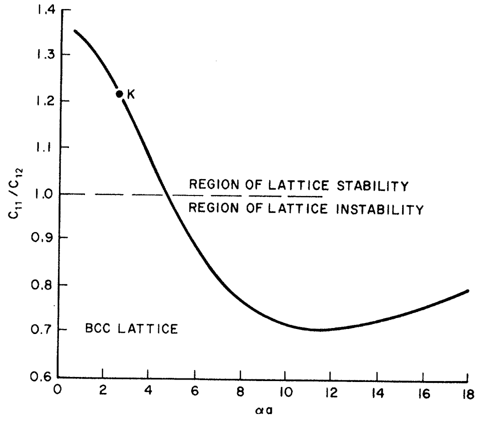

FIG. 2. Ratio of elastic constants $C_{11}/C_{12}$ versus $\alpha a$ for Morse-function bcc lattices. An experimental value of $C_{11}/C_{12}$ is indicated for potassium; values of $C_{11}/C_{12}$ for other bcc metals do not lie within the range of values attainable with the Morse function. The Born stability criteria are satisfied for values of $\alpha a$ less than 4.8 only.

$$r_I - r_0 = (\ln 2)/\alpha \ . \tag{25}$$

Dividing Eq. (25) by the lattice parameter $a$ and requiring that $\alpha a < 4.8$ leads to the conclusion that

$$r_I - r_0 > (a \ln 2)/4.8 \tag{26}$$

for the Morse-function bcc lattice to be stable.

The above results are in agreement with Born's suggestion that the fcc lattice with two-body central force interactions is stable throughout while the bcc lattice is stable only when $r_I - r_0$ is relatively large. The present results are also complementary to those of Misra, discussed earlier in this paper.

Morse functions have been used to investigate the elastic constants of solids,[4-6] and are often used to calculate other properties of solids which are intimately connected with elastic properties.[4, 7-9] Thus, it is of practical interest to determine whether or not a Morse-potential cubic crystal, which is intended in some sense to represent an actual crystal, can possess the proper (i.e., experimental) values of the elastic constants $C_{11}$ and $C_{12}$. Figures 1 and 2 show that a cubic Morse-function crystal lattice cannot take on arbitrary values of the elastic constants $C_{11}$ and $C_{12}$. In particular, for the fcc lattice, $C_{11}/C_{12}$ appears constrained to lie within about 1.14 and 2.00, whereas for the bcc lattice, $C_{11}/C_{12}$ does not exceed about 1.36.

Girifalco and Weizer,[4] in their study of the application of Morse functions to cubic metals, determined the Morse-function parameters $\alpha a$, $\alpha r_0$, and $D$ (for several metals) from the equilibrium condition, Eq. (7), and from experimental values of cohesive energy and compressibility. The values of $\alpha a$ which they determined and the resulting values of $C_{11}/C_{12}$ are listed in the last two columns of Tables I and II. It is noted that the values of $C_{11}/C_{12}$ calculated by Girifalco and Weizer are in agreement with the values determined from the curves of Figs. 1 and 2, for the particular values of $\alpha a$ used in their study. The second, third, and fourth columns list experimental values

TABLE I. Values of $\alpha a$ for Morse-function fcc crystal lattice and experimental values of elastic constants $C_{11}$ and $C_{12}$ for fcc metals. Elastic constants (Refs. 22, 23) are for 0 °K.

| Metal | $C_{11}$ ($10^{12}$ dyn/cm$^2$) | $C_{12}$ ($10^{12}$ dyn/cm$^2$) | $C_{11}/C_{12}$ Expt | $\alpha a$ determined from expt value of $C_{11}/C_{12}$ | $\alpha a$, as determined in Ref. 4 | $C_{11}/C_{12}$ calculated in Ref. 4 |
|---|---|---|---|---|---|---|
| Al | 1.143 | 0.619 | 1.847 | 10.979 | 4.694 | 1.398 |
| Ni | 2.612 | 1.508 | 1.732 | 8.766 | 5.000 | 1.425 |
| Cu | 1.762 | 1.249 | 1.411 | 4.842 | 4.900 | 1.416 |
| Ag | 1.315 | 0.973 | 1.351 | 4.183 | 5.576 | 1.478 |
| Pd | 2.341 | 1.761 | 1.329 | 3.929 | | |
| Pb | 0.555 | 0.454 | 1.222 | 2.534 | 5.842 | 1.502 |
| Au | 2.016 | 1.697 | 1.188 | 1.944 | | |

TABLE II. Values of $\alpha a$ for Morse-function bcc crystal lattice and experimental values of elastic constants $C_{11}$ and $C_{12}$ for bcc metals. Elastic constants (Refs. 22, 23) are for 0 °K except as noted.

| Metal | $C_{11}$ ($10^{12}$ dyn/cm$^2$) | $C_{12}$ ($10^{12}$ dyn/cm$^2$) | $C_{11}/C_{12}$ Expt | $\alpha a$ determined from expt value of $C_{11}/C_{12}$ | $\alpha a$, as determined in Ref. 4 | $C_{11}/C_{12}$ calculated in Ref. 4 |
|---|---|---|---|---|---|---|
| Cr | 3.5 | 0.7 | 5.0 | | 4.520 | 1.026 |
| Mo | 4.80 | 1.65 | 2.91 | | 4.736 | 1.016 |
| W | 5.326 | 2.049 | 2.599 | | 4.450 | 1.032 |
| V | 2.324 | 1.194 | 1.946 | | | |
| Fe | 2.432 | 1.381 | 1.761 | | 3.976 | 1.111 |
| Ta | 2.663 | 1.582 | 1.683 | | | |
| Nb | 2.48 | 1.53 | 1.62 [a] | | | |
| Na | 0.95 | 0.62 | 1.53 [b] | | 2.534 | 1.232 |
| K | 0.0416 | 0.0341 | 1.220 | 2.606 | 2.586 | 1.223 |

[a] Elastic constants are at room temperature.

[b] Elastic constants are at 80 °K.

of $C_{11}$, $C_{12}$, and $C_{11}/C_{12}$; the fifth column gives the values of $\alpha a$ which correspond to the experimental values of $C_{11}/C_{12}$. These points, i.e., ($C_{11}/C_{12}$, $\alpha a$), are also indicated on the curves of Figs. 1 and 2; the values of $\alpha a$ should be of interest in applications of Morse functions involving calculations of the behavior of a crystal in the presence of uniaxial stresses or strains (see, e.g., Refs. 7-9), i.e., in cases where it is important that the linear stress-strain relations of the Morse-function crystal be in agreement with the experimental relations.

For all fcc metals for which experimental values of $C_{11}$ and $C_{12}$ were available, the ratio $C_{11}/C_{12}$ was greater than 1.14 and less than 2.0; i.e., this ratio falls within the range of values of $C_{11}/C_{12}$ attainable in Morse-function fcc crystals. Thus, for each of these cases a Morse-function fcc lattice can be devised (i.e., values of $\alpha a$, $D$, and $\alpha r_0$ may be specified, $\alpha a$ being determined by Fig. 1) which exhibits the experimental values of $C_{11}$ and $C_{12}$. For the bcc metals for which experimental values of $C_{11}$ and $C_{12}$ could be found, however, only potassium has a ratio $C_{11}/C_{12}$ which lies within the range attainable with Morse functions. Thus, in general, the Morse-function bcc lattice is not capable of exhibiting the correct (i.e., experimental) elastic constants $C_{11}$ and $C_{12}$ for bcc metals, potassium being an exception.

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*Resident Consultant to The RAND Corp. Member of the Professional Staff, The Rand Corp., at initiation of this work and member of the faculty, School of Engineering and Applied Science, University of California, Los Angeles, at completion of this work.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 2 15 JULY 1970

# Polarizability and Two-Quantum Excitations in Alkali Halides and Deep Impurity States in Rare-Gas Solids

Jean Heinrichs*
*Institut de Physique*, *University of Liège*, *Sart-Tilman*, *Belgium*†

*and*

*IBM Watson Laboratory*, *Columbia University*, *New York*, *New York* 10025

(Received 6 January 1970)

The general theory of the electronic dielectric constant of crystals, developed in a previous paper in the framework of an individual-ion model, is analyzed for diatomic systems. Use is made of an effective two-state model for the individual atoms. An exception is made, however, for certain terms in the polarizability which depend very strongly on the higher excited states, whose effect is thus taken into account, in an average-excitation-energy approximation. The final result of this analysis is a simplified expression for the frequency-dependent polarizability of an individual atom in the crystal, which includes explicitly the quantum correction arising from the induced dipole-dipole interaction. In a first application of these results, we carry out a detailed study of the static polarizability of alkali halide crystals, on the basis of a reasonable assumption for the polarizability of a free ion in an excited state. The dipole-dipole correction in the polarizability is found to be positive and to vary from 2 to 8%. This effect is in good quantitative agreement with a correction which has been derived from an empirical analysis of dielectric-constant data for the alkali halides. For the effects of frequency dispersion in the polarizability, we also find reasonable agreement with similar empirical results for the alkali halide ions. As a second type of application, we consider the problem of deep impurity states in crystals. An explicit expression for the electronic frequency shift of a substitutional impurity is obtained from the study of the singularities of the polarizability. In particular, this leads to a simple expression for the van der Waals constant for an excited impurity interacting with a matrix atom in the ground state. Application of this formula to rare-gas and molecular impurities in rare-gas matrices leads to surprisingly good agreement with empirical results, as obtained from an analysis of experimental shifts in terms of 6-12 potentials. As a last application we study the oscillator strength of two-quantum excitations (double excitons), which arise as a consequence of the quantum dipole fluctuations. For the alkali halides we find that this oscillator strength ranges from 4.5 to 20% of that of the ordinary one-quantum excitations in the NaCl structure, while rising to 30% in the CsCl structure.

## I. INTRODUCTION

Theoretical and experimental studies of electronic excited states of the alkali halides and rare-gas solids seem to indicate that the model of tight-binding excitons, as developed originally by Frenkel, does not provide an adequate description of the electronic states in these systems. Most of these investigations were started, in fact, after the unexpected finding that the electronic spectra of the pure rare-gas solids can be interpreted rather well in terms of the Wannier model, which describes the opposite limit of loosely bound excitons of large radii.[1] This provided strong evidence, of course, for non-negligible effects associated with the overlap of the charge distributions of neighboring atoms or ions in these crystals, especially in excited states. It has led to numerous attempts to improve the extreme tight-binding approximation by taking overlap and exchange effects into account, in addition to the Coulomb interaction. In this improved form, the tight-binding approximation has been rather successful in predicting exciton energies in the pure rare gases[2,3] as well as excitation energies of impurities in solid He, Ne,