PHYSICAL REVIEW B VOLUME 16, NUMBER 6 15 SEPTEMBER 1977

Temperature dependence of the elastic shear moduli of the cubic metals

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(Received 11 April 1977)

A theoretical model for the temperature dependence of the elastic shear moduli of the cubic metals is presented which accounts for the quantitative relationship of these elastic properties to the thermal expansion. The particular phenomenon which the model is concerned with is the extremely rapid temperature variation of the shear moduli, which typically is about 25 times as great as the rate of thermal expansion. The model has the following salient features: (i) The interatomic pair pseudopotential is approximated over the important thermal range by means of a Morse potential; (ii) the thermal expansion is assumed to arise from anharmonic Morse oscillators which are further assumed not to be significantly coupled to each other; (iii) the exact quantum-mechanical solutions for the Morse oscillators are then combined with the Debye model to give an analytic formula for the thermal expansion; (iv) the elastic shear moduli are calculated from this, assuming nearest-neighbor interactions only. The calculated thermal expansions are found to agree quite well with the experimental values, particularly at low temperatures. The rapid temperature variation of the shear moduli is explained by the model in terms of the thermal movement of the nearest neighbors with respect to the interatomic-potential minima. Complete agreement between calculated and experimental shear moduli has been limited, however, by the contributions beyond the nearest neighbors which are not zero, and which have not been included in the formulas.

I. INTRODUCTION

Because the temperature dependences of the elastic moduli of materials are an important manifestation of their mechanical and thermodynamic properties, a number of theoretical investigations have been made in an attempt to gain a basic understanding of the mechanisms underlying the observed elastic behavior. Many of these have centered their attention on the shear moduli of the cubic metals because of the relative simplicities possible in their analysis. These investigations have started from several different points of view, which include among others the thermodynamic equation of state,[1] the quasiharmonic-anisotropic-continuum model,[2] and the inclusion of anharmonic contributions in the interatomic potential.[3]

All of these studies have accounted for the general functional form of the temperature dependences of the shear moduli. It has been known for some time that the shear moduli of most cubic metals decrease with increasing temperature. The temperature dependence is linear for moderate temperatures, while the variation is as T^4 at low temperatures. However, there is one quite striking aspect to this temperature variation which has apparently received very little attention so far, and that is the large magnitude of the variation. Between 0 °K and room temperature, for example, the variation for most cubic metals is typically about 25 times as great in magnitude as the rate of thermal expansion, and may represent a percent change of 10% to 20% or more.

It appears unlikely that an explanation of this large temperature variation is possible unless it is made within the framework of a realistic model of the thermal behavior of the interatomic potential. If the anharmonicity is merely included in an *ad hoc* way, then the magnitude of the variation can be accounted for only by an adjustable constant.[3] Most treatments of the interatomic potential have involved empirical calculations of the harmonic force constants. These can be related to the elastic moduli, but not to their temperature dependence unless anharmonic contributions are introduced in the interatomic potential.

One of the early force-constant calculations for the cubic metals was made by De Launay.[4] This calculation used Born's method of long waves to relate the nearest-neighbor and next-nearest-neighbor force constants to the elastic moduli. In addition, De Launay attempted to explain the failure of the Cauchy condition in cubic metals. This condition, which states that in cubic crystals, $C_{12}=C_{44}$, should be obeyed if equilibrium is maintained by central pairwise forces only. De Launay assumed that the difference between these two elastic moduli is not zero because it equals the bulk modulus of the electron gas. This calculation has been criticized by Thomas[5] who pointed out that the method of long waves cannot be used with De Launay's model since it assumes periodic boundary conditions, and hence, constant volume. Instead, he argued that the pressure as well as the bulk modulus of the electron gas must be included in the calculation, since the crystal is not in equilibrium under pair forces alone.

Another problem with this type of calculation

concerns the form of the central pair potential. In De Launay's formulation, one of the shear moduli in the bcc case and the difference between the two shear moduli in the fcc case arise from the next-nearest-neighbor force constant only. However, recent theoretical work on the metallic pseudopotential[6,7] raises some serious questions with this formulation. Not only is the potential minimum not generally centered at the nearest neighbor, but the potential, itself, decreases very rapidly in magnitude beyond the nearest neighbor with an oscillatory behavior which falls off asymptotically as the inverse cube of the distance. This means that the contributions from beyond the nearest neighbors are small if not negligible, and do not adequately account for the shear strengths of these metals.

Consequently, it is evident that a satisfactory explanation of the temperature dependence of the shear moduli of the cubic metals must be consistent with the requirements of lattice stability and the nature of the pair pseudopotential, incorporating its anharmonic properties in a natural way rather than in an add-on fashion. In this work, we will meet these requirements by approximating the pseudopotential over the important thermal range by means of a Morse potential. We will further assume the existence of nearly independent Morse oscillators analogous to the normal modes of the harmonic case. The problems inherent in the De Launay approach will be avoided by computing the shear moduli directly from the pair potential by means of Fuchs's method of homogeneous deformation.[8] Certain assumptions will then be made about the thermal variation of the interatomic potential which makes possible a calculation of the thermal expansion and the temperature dependence of the shear moduli. The calculations show good quantitative agreement with the observed thermal expansions, particularly at low temperatures, and also account for the very large temperature variation of the shear moduli compared to the thermal expansion. The success of the calculations strongly support the model used for the thermal variation of the interatomic potential.

II. THERMAL BEHAVIOR OF THE INTERATOMIC POTENTIAL

If we begin by approximating the pair pseudopotential with a Morse potential over the range where the thermal effects that we are considering are important, and further assume that the coupling between the Morse oscillators is unimportant in these effects, we must still determine the behavior of this potential as a function of temperature. The pseudopotentials which have been calculated for these metals are valid only for a specific temperature. While it is possible to calculate pseudopotentials for different temperatures, we will see that the actual thermal variation of the interatomic potential is quite small, making this an extremely difficult way to proceed. Instead, we will draw some inferences about the temperature variation that will allow us to proceed toward an analytic solution of the problem in a considerably simpler manner.

A rather detailed discussion of the interatomic metallic pseudopotential in real space has been given by Finnis[9] who points out that this potential accounts for only a small part of the crystalline cohesive energy. In spite of this, the calculation of the bulk modulus appears to involve only this contribution to the total energy, and furthermore ignores its implicit volume dependence entirely. Finnis explains this paradoxical situation in a way that is quite useful to the understanding of the thermal properties we are considering. The other contribution to the energy, which is the dominant one and is called $F(V)$ by Finnis, has a very weak volume dependence. In the "pseudoatom" approximation, in which an ion plus its spherical screening cloud of z conduction electrons overlaps with other neutral pseudoatoms to constitute the metal, this volume dependence does not exist at all.

The value of the pseudoatom picture lies partly in its simplicity, since this decomposition of the charge density means that if an ion is displaced, the resulting charge redistribution is simply obtained by a rigid displacement of the whole pseudoatom. But more important is the fact that the pseudoatom picture is equivalent to second-order perturbation theory, and in this approximation, all of the second-order energy change under a distortion only involves the pseudopotential calculated at constant density. Finnis describes some of the difficulties with calculating the bulk modulus using the method of long waves and this approximation, but the important point is that these are associated with higher-order corrections which come about when the pseudoatoms change their size and shape as the metal is dilated or compressed. The phenomenon most sensitive to these higher-order corrections is the breakdown of the Cauchy relation in cubic crystals, since this involves a considerable amount of electron screening.

These difficulties do not enter into the calculation of the shear moduli at a given temperature, since these involve only homogeneous strains at constant volume. However, in analyzing the changes in the shear moduli with temperature and the accompanying volume changes, some way of accounting for changes in the shear moduli with

changing volume is necessary. In examining the phenomenon of thermal expansion in the pseudoatom picture, it is evident that linear expansion with increasing temperature can arise from the asymmetrical nature of the interatomic potential alone. Noting further the weak volume dependence of $F(V)$, one can infer that the dominant contribution to the thermal expansion comes from the interatomic potential. In this picture, thermal expansion arises from the asymmetrical interaction of the rigid pseudoatoms undergoing thermal motion. The deformations of the pseudoatoms brought about by their mutual interactions are not included in this picture, but these presumably involve relatively small contributions to the effect.

In keeping with this picture, it is reasonable to assume that the thermal motion of the rigid pseudoatoms is described by uncoupled anharmonic oscillators whose energy distribution is given by the Debye model. There is a rather obvious test of these assumptions that can be made from thermal expansion data. It is generally known that any anharmonic potential can be expanded in a Taylor series about its minimum, and at low temperatures, the lowest order or harmonic term is dominant. If the next term in the expansion, the cubic term, is taken as a perturbation on the harmonic contribution, it is easy to show that the displacement of the equilibrium position for a given quantum state is proportional to the principal quantum number and the frequency of oscillation. This description should be valid at low temperatures. Furthermore, it is interesting to note that this functional form for the displacement is the same, except for multiplicative constants, as that of the energy in the harmonic approximation. What this means is that if this result is coupled with the Debye model and the assumption of independent anharmonic oscillators as a model of linear thermal expansion, then the functional form of the coefficient of thermal expansion should be the same (except for constant factors) as that for the specific heat.

It is a simple matter, then to compare the coefficient of linear thermal-expansion curves with those for the specific heat. Generally, for the cubic metals one finds that at low temperatures they are quite similar. It is only at higher temperatures, where the specific heat levels off and the coefficient of linear thermal expansion continues to increase that they begin to differ appreciably. Although these qualitative observations tend to confirm the assumptions that we have made so far, a quantitative comparison of the experimental data with a calculation using the Morse potential should provide a more definitive test of these assumptions.

III. CALCULATION OF THE THERMAL EXPANSION

To test the assumptions that we have made so far, we assume that the anharmonic part of the pseudopotential can be adequately represented over the important thermal range by the Morse potential

$$V(r) = D(1 - e^{-a(r - r_0)})^2, \tag{1}$$

where D is the dissociation energy, r_0 is the position of the potential minimum, and a is an inverse width of the potential. From this, we wish to develop an analytic formula for the thermal expansion that can be quantitatively compared with experiment. Because r_0 does not generally equal r_n, the nearest-neighbor distance, we introduce a new variable x which is defined by the relation $r_0 = r_n(1 - x)$. The separation between the potential minimum and the nearest-neighbor position is then xr_n which may be either positive or negative.

According to the assumptions that we have made so far, the pseudopotential at constant density should provide an accurate description of the thermal effects that we are considering. This means that in terms of the Morse potential approximation, the parameters D, a, and r_0 are independent of temperature. The primary thermal effect, then, is the movement of the nearest-neighbor position with respect to the potential minimum. One can see intuitively that while thermal expansion produces relatively small changes in r_n, the corresponding changes in the quantity x are quite large because of the greatly magnified effect which small changes in r_n have on this quantity. It is these large thermal changes in $x(T)$ that one might guess to be the origin of the large thermal variation in the elastic shear moduli.

For the moment, however, we are interested in applying these assumptions to the calculation of the thermal expansion. If this is assumed to arise from the anharmonicity of the interatomic potential alone, then it can be calculated directly from a thermal average of the equilibrium positions of the bound states of the potential. For the Morse potential, the energies and wave functions of these bound states are known exactly, and from these the corresponding displacements can also be determined exactly. Since we will neglect the effect of any rotational motion, the vibrational energy for principal quantum number m is given by[10]

$$E_m = \hbar\omega(m + \tfrac{1}{2}) - (\hbar^2\omega^2/4D)(m + \tfrac{1}{2})^2, \tag{2}$$

where $\omega = a(2D/\mu)^{1/2}$ is the frequency of small oscillations. For the equilibrium positions of the bound states, we need an expression such as was discussed earlier that is valid at low temperatures

(small quantum numbers). In the Appendix, it is demonstrated that the average value of the radius for the bound state of quantum number m is

$$\langle r_m \rangle = r_0 + (\hbar\omega/2aD)(m + \tfrac{3}{4}) + O(\omega^2) \tag{3}$$

for the Morse potential (1). In the special case of the Morse potential, contributions of first and second order only in ω are an accurate description for virtually all the bound states because of the sharp cutoff introduced by the exponential. The contribution of first order in ω is the one we are interested in for the thermal expansions at low temperatures. By way of a comparison, if the potential (1) is expanded in a Taylor series and the cubic term is taken as a perturbation on the harmonic term first-order perturbation theory yields the result that $\langle r_m \rangle = r_0 + 5(\hbar\omega/4aD)(m + \frac{1}{2})$.

Before going further, we must first carefully examine how we will interpret Eq. (3) in our calculation. Strictly speaking, Eqs. (2) and (3) refer to the fixed frequency and energy levels of a given Morse potential. But in our assumption of the existence of independent or uncoupled Morse oscillators, we must be careful not to identify these with the interatomic potential, since the fixed frequency of this potential cannot lead to a frequency spectrum. Instead, we are assuming the existence of nearly independent Morse oscillators which are comparable to the normal modes of the harmonic approximation. By analogy with the harmonic case, Eq. (3) is interpreted as representing the displacements associated with these independent Morse oscillators and which make up the anharmonic frequency spectrum. Conceptually, this idea may be pictured in the following way. In the harmonic approximation, the energy levels of the system are not those of the individual interatomic potentials (or the "springs" connecting the mass points), but rather are determined by the frequencies of the normal modes. The energy associated with a given normal mode can be connected with an average root-mean-square deviation of the "springs" from equilibrium which is small for a long wavelength and large for a short wavelength. The exact relationship is determined by the force constants of the individual springs, which in turn are determined by the energy levels and frequencies of free oscillation of the individual interatomic potentials. It seems reasonable to connect, in similar fashion, the asymmetrical movement of anharmonic "springs" for a given mode of oscillation with a net displacement associated with the "Morse force constant" or, alternatively, the frequency of small, free oscillations associated with the Morse potential. The interpretation of Eq. (3) in this manner seems reasonable from this conceptual viewpoint and is consistent with the success of the quasiharmonic model. This assumption is necessitated by the lack of any appropriate mathematical method for dealing with anharmonic forces, but as will be seen later, it yields excellent agreement with experimental results.

We now wish to calculate the thermal average of (3) for an individual Morse oscillator which is valid for small quantum numbers. Using the terms of first order in ω only in (2) and (3), the thermal average

$$\bar{r} = \sum\nolimits_m \langle r_m \rangle e^{-E_m/kT} \Big/ \left(\sum\nolimits_m e^{-E_m/kT} \right)$$

can be determined in complete analogy with the thermal average of the harmonic oscillator energy, making use of results such as $\sum_{n=0}^{\infty} e^{-nx} = (1 - e^{-x})^{-1}$ and $\sum_{n=0}^{\infty} n e^{-nx} = e^x(e^x - 1)^{-2}$. The result is

$$\bar{r} = r_0 + \frac{3\hbar\omega}{8aD} + \frac{\hbar\omega}{2aD}(e^{\hbar\omega/kT} - 1)^{-1}, \tag{4}$$

where the second term is the contribution of the zero-point displacement.

The next step in the calculation of the thermal expansion is the averaging of (4) over the frequency distribution of the crystal. The average is only taken over the third term on the right-hand side of (4), which in the Debye approximation is given by

$$\langle \bar{r} \rangle = \frac{1}{3N} \int_0^{\omega_D} \frac{9N}{\omega_D^3} \omega^2 d\omega \, \frac{\hbar\omega}{2aD} (e^{\hbar\omega/kT} - 1)^{-1}. \tag{5}$$

We can see that the thermal average in (5) is proportional to the harmonic energy in agreement with Grüneisen's rule. The thermal expansion according to (5) can now be calculated in a manner completely analogous to the calculation of the energy in the harmonic approximation. Letting $x = \hbar\omega/kT$ and $x_D = \Theta_D/T$, one finds that

$$\langle \bar{r} \rangle = (3kT/2aD)(T/\Theta_D)^3 f(x_D), \tag{6}$$

where

$$f(x_D) = \int_0^{x_D} \frac{x^3 \, dx}{e^x - 1}$$

and Θ_D is the Debye temperature. The linear thermal expansion according to this model is given by $\langle \bar{r} \rangle / r_n$. The coefficient of linear thermal expansion $\alpha(T)$ is simply the temperature derivative of this quantity as given by (6), i.e.,

$$\alpha(T) = \frac{d\langle \bar{r} \rangle / r_n}{dT} = \frac{3k}{2aDr_n} \left(\frac{T}{\Theta_D} \right)^3 g(x_D), \tag{7}$$

where

$$g(x_D) = \int_0^{x_D} \frac{x^4 e^x \, dx}{(e^x - 1)^2}.$$

It is evident from (6) and (7) that this model yields a linear thermal expansion that has the same functional form as the energy in the harmonic approximation, and furthermore, that $\alpha(T)$ has the same functional form as the specific heat in the Debye approximation. In addition, it is evident that these two formulas give these two quantities in terms of the product of two unknowns: the depth of the potential well and its inverse width in units of the inverse nearest-neighbor distance, ar_n. This product of the width and depth of the potential is the only unknown parameter, and thus can be determined by a single experimental value of either the linear thermal expansion or $\alpha(T)$ at a particular temperature.

Comparing these analytical formulas with experimental data is therefore a simple matter, since it requires only the evaluation of a single parameter from the data. For this purpose the critical compilation of thermal expansion data of Touloukian *et al.* was used, and for consistency, the total per cent thermal expansion from 0 °K up to room temperature (293 °K) was used to evaluate Dar_n. Comparison of the experimental data with the analytical formulas showed excellent agreement for a large number of cubic metals, particularly at low temperatures. Comparison of the theoretical curve and experimental values of $\alpha(T)$ for copper is illustrated in Fig. 1. As can be seen, the agreement is excellent up to room temperature, and confirms the conjecture that the $\alpha(T)$ curve has the same functional form as the specific heat at low temperatures. At higher temperatures, the theoretical curve levels off, as does that for the specific heat, while the experimental points continue to take on higher values. This is because the terms which are quadratic in the frequency, which have not been included in the theoretical formula, take on greater and greater importance at higher temperatures. The agreement illustrated for copper is comparable to that found for other metals.

A test of this explanation of the deviations at higher temperatures is easily made in the case of metals which have deep potential wells. Such metals are characterized by small thermal expansions and large shear moduli. For such metals, the "low temperature" behavior should extend to relatively high temperatures because the greater depth of the well makes the linear behavior extend over a greater range of energies. Although the thermal expansion data alone do not yield a value for the depth of the well, we will see later, from values obtained from the shear moduli, that such a trend is apparent. In the case of tungsten, for example, which has a deep well, the "low temperature" behavior extends to approximately 1000 °K.

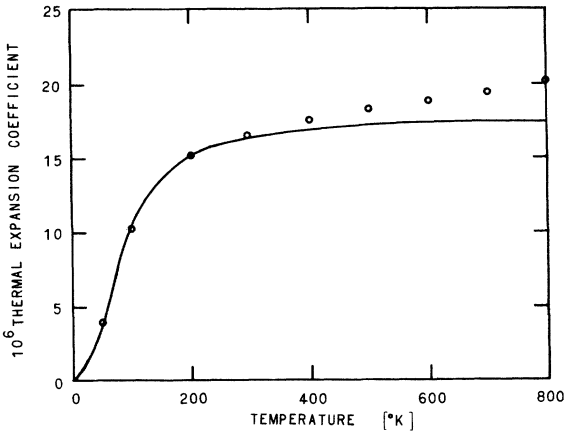

FIG. 1. Calculated (solid line) and observed values for copper of the temperature variation of the coefficient of thermal expansion.

This calculation has demonstrated that assumptions which have been made so far are consistent with the experimental thermal expansion data. Furthermore, the close agreement between theory and experiment strongly suggests the validity of these assumptions. While the high-temperature behavior of the thermal expansion data could in principle be treated theoretically by including the contributions of the terms which are quadratic in the frequency, such a treatment is not particularly important to the main problem at hand, which is the confirmation of the proposed thermal model to be used in the calculation of the elastic shear moduli.

IV. CALCULATION OF THE ELASTIC SHEAR MODULI

We saw earlier that the quantity $x(T)$, which is the fractional separation between the nearest-neighbor distance and the potential minimum, is a very sensitive function of changes in r_n. Since in the thermal model that we are using the potential parameters are independent of temperature, then the changes in $x(T)$ brought about by thermally induced changes in r_n provide the basic mechanism for the large temperature-dependent changes in the shear moduli. The next step in the analysis is the incorporation of this mechanism into an analytical representation of these temperature changes.

The shear moduli C_{44} and $C' = \frac{1}{2}(C_{11} - C_{12})$ for the cubic metals can be expressed in terms of the first and second derivatives of the interatomic potential, evaluated at the nearest-neighbor distance, by means of the method of homogeneous deformation.[8] The expressions for the fcc lattice are

$$C' = \tfrac{1}{4}[7r_n V'(r_n) + r_n^2 V''(r_n)],$$

$$C_{44} = \tfrac{1}{2}[3r_n V'(r_n) + r_n^2 V''(r_n)],$$

and for the bcc lattice

$$C' = \tfrac{4}{3} r_n V'(r_n),$$

$$C_{44} = \tfrac{4}{9}[2r_n V'(r_n) + r_n^2 V''(r_n)].$$

These expressions include nearest-neighbor interactions only, and give the shear moduli in units of energy per ion. Because the contributions from beyond the nearest neighbors are generally small, they will not be included in the analysis. Some of the consequences of this approximation will be discussed later.

These formulas for the shear moduli of the two cubic structures can be expressed in terms of the Morse potential (1). The result is

$$C_{44} = Dar_n e^{-axr_n}[3(1 - e^{-axr_n}) + ar_n(2e^{-axr_n} - 1)], \quad (8)$$

$$C' = \tfrac{1}{2} Dar_n e^{-axr_n}[7(1 - e^{-axr_n}) + ar_n(2e^{-axr_n} - 1)], \quad (9)$$

for the fcc structure and

$$C_{44} = \tfrac{8}{9} Dar_n e^{-axr_n}[2(1 - e^{-axr_n}) + ar_n(2e^{-axr_n} - 1)], \quad (10)$$

$$C' = \tfrac{8}{3} Dar_n e^{-axr_n}[1 - e^{-axr_n}], \quad (11)$$

for the bcc structure, where the equations have been expressed in terms of the variable $x = (r_n - r_0)/r_n$. Before proceeding to quantitative considerations, there are several qualitative observations that can be made from these equations. First, we can see that the ratio of the two shear moduli $\beta = C_{44}/C'$, which is usually known as the anisotropy factor, is dependent upon several things. The most important is structure, since it is quite evident that this ratio takes on quite a different form for the bcc structure than for the fcc structure. Another important factor is the position of the potential minimum with respect to the nearest neighbor. If the potential minimum lies inside the nearest neighbor ($x > 0$), then the ratio has a value less than 2 in the case of the fcc structure. On the other hand, if the potential minimum lies outside the nearest neighbor ($x < 0$), then β is greater than 2. Only in the special case when the potential minimum is exactly at the nearest neighbor [$x = 0$, and $V'(r_n) = 0$] is the ratio exactly equal to 2. Most fcc metals fall into the second category, although aluminum is a notable exception.

In the case of the bcc structure, the stability condition $C' > 0$ requires that the potential minimum lie inside of the nearest neighbor. Although β is not strongly dependent on the temperature in most fcc metals, it can be seen from (10) and (11) that β is generally quite strongly temperature dependent in the bcc metals unless $V''(r_n) = 0$. None of the bcc metals investigated was found to obey this criterion, although iron comes closest. Interestingly, iron is known to undergo two phase transformations at elevated temperatures (1185 and 1667 °K), which would be consistent with a change in sign in $V''(r_n)$ for bcc iron above room temperature. From these qualitative considerations, it is evident that the magnitude and temperature dependence of the anisotropy factor in cubic metals is a function not only of the structure, but also of the details of the interatomic potential and its relative position with respect to the nearest neighbors.

It is apparent that there are three unknowns in Eqs. (8), (9), (10), and (11), namely D, a (or ar_n), and x, corresponding to the three parameters specifying the Morse function. These three parameters can be evaluated from three experimental values of the two elastic shear moduli, (one evaluated at two different temperatures) or alternatively, from two values of the elastic shear moduli and the value of Dar_n obtained from the thermal expansion data. In principle, these two methods should be equivalent if the theory is correct, but in practice, we will see that in some cases, the approximations used so far favor the second approach over the first for a practical evaluation of the parameters.

The evaluation of these three parameters should not only give the important dimensions of the pseudopotential well but also the temperature dependence of the shear moduli. Before proceeding with this part of the calculation, we will first derive analytical formulas for the temperature dependence. These will be used to show the origin of the large thermal variation as well as for the numerical evaluation of the parameters. To begin, there are two quantities in Eqs. (8)–(11) that vary with the temperature according to the thermal model used here. The first is r_n which increases with increasing temperature according to the thermal expansion relation. The second is the quantity x which we have already seen varies rapidly with the temperature. For simplicity, we will discuss the variation of these quantities with respect to 0 °K. Since

$$r_n(T) = r_n(0)(1 + \Delta r/r_n) \quad (12)$$

to first order in $\Delta r/r_n$, the temperature dependences of the shear moduli will be expressed as functions of this quantity. Since $x(T)$ occurs in Eqs. (8)–(11) only in the exponentials, expressions for their temperature dependence are needed. Making use of (12) and the definition of x, one obtains the result

$$e^{-ax(T)r_n(T)} = e^{-ax(0)r_n(0)}[1 - ar_n(\Delta r/r_n)]. \quad (13)$$

Unless otherwise specified, the quantities x and

r_n are the values at 0°K in the above formulas and those which follow.

The relative magnitude of the temperature dependence of $x(T)$ can now be seen by combining (12) with its relation with r_0 and r_n or by taking logarithms of both sides of (13). The result is

$$x(T) = x(0) + \Delta r/r_n . \tag{14}$$

Therefore the change in xr_n is exactly the same as that in r_n but since the first quantity is such a small fraction of the second in most cases, the percent change is very large by comparison. We may now use these relations to derive the change with temperature of the shear moduli with respect to their values at 0°K (or any other arbitrary fixed temperature). Keeping terms of only first order in $\Delta r/r_n$, one obtains the results

$$\frac{\Delta C_{44}(T)}{C_{44}(0)} = -ar_n(\Delta r/r_n) \times \{1 + 2/ar_n + (e^{-axr_n}/\Gamma) \times [e^{-axr_n}(2ar_n - 3) - (2e^{-axr_n} - 1)]\}, \tag{15}$$

$$\frac{\Delta C'(T)}{C'(0)} = -ar_n(\Delta r/r_n) \times \{1 + 2/ar_n + (e^{-axr_n}/\Gamma') \times [e^{-axr_n}(2ar_n - 7) - (2e^{-axr_n} - 1]\}, \tag{16}$$

for the fcc structure and

$$\frac{\Delta C_{44}(T)}{C_{44}(0)} = -ar_n(\Delta r/r_n) \times \{1 + 2/ar_n + (8e^{-axr_n}/9\Gamma) \times [2e^{-axr_n}(ar_n - 1) - (2e^{-axr_n} - 1)]\}, \tag{17}$$

$$\frac{\Delta C'(T)}{C'(0)} = -ar_n(\Delta r/r_n)[1 + 2/ar_n - 16e^{-2axr_n}/3\Gamma')], \tag{18}$$

for the bcc structure, where $\Gamma = C_{44}(0)/Dar_n$ and $\Gamma' = 2C'(0)/Dar_n$. These four equations include the small correction for the thermal variation of the volume in order to make a comparison with experimantal data more convenient.

There are several things that are immediately evident from these equations. First, there is only one temperature-dependent quantity on the right-hand side of these equations which determines the fractional change in the elastic moduli with temperature, namely, the linear thermal expansion $\Delta r/r_n$. This means that the functional form of the temperature dependence is determined by that of the thermal expansion. From Eq. (6), it can easily be deduced that this behavior is linear at high temperatures and varies as T^4 at low temperatures, in accord with observation. Moreover, since the quantities in curly brackets on the right-hand side of the equations are generally positive [with the possible exception of Eq. (18) which will be discussed later], the negative sign in each of the equations correctly indicates that the elastic moduli decrease with increasing temperature.

The most important property of the equations, however, is the fact that the magnitude of the temperature change is related to physical parameters of the potential function. The leading factor in each equation is the quantity ar_n which is the inverse of the fraction of r_n that equals the width of the potential well. For example, if the width of the potential is a tenth of r_n, then $ar_n = 10$. Since the width of the potential well is typically a small fraction of r_n, this factor by itself introduces an order-of-magnitude percent change in the elastic moduli compared to the thermal expansion. Generally, the quantities inside the curly brackets are greater than 1, so that these introduce an even greater change in the elastic moduli compared to the thermal expansion. Consequently, the equations account for the large thermal variation of the shear moduli as well as the functional dependence with temperature. Clearly, the detailed form of the equations depends on the specific form of the Morse potential which was assumed to approximate the actual interatomic potential. However, it seems reasonable to assume that the factors which have been found to be important for the temperature variation of the elastic moduli, particularly the rapid variation of $x(T)$ which with the Morse potential yields a multiplicative factor ar_n in the temperature variation, would also be the basic mechanism arrived at with a different anharmonic potential.

In order to compare the above equations with experimental results, it is necessary to deduce values for the three parameters which characterize the potential. One way of accomplishing this is to take three experimental values for the two shear moduli and fit these to Eqs. (8) and (9) or (10) and (11), depending on the structure. When this calculation was carried out, two problems arose which are attributable to the approximations which have been used. First, it was found that it was not possible to simultaneously fit the theoretical curves to the experimental points of both shear moduli. In addition, it was found that when the best compromise fit was made, the values of Dar_n obtained from the calculation were usually inconsistent with the values obtained from the thermal expansion data, sometimes by large amounts.

The reasons for these difficulties can be seen by referring to Fig. 2, where the potential functions for aluminum are displayed. In the case of

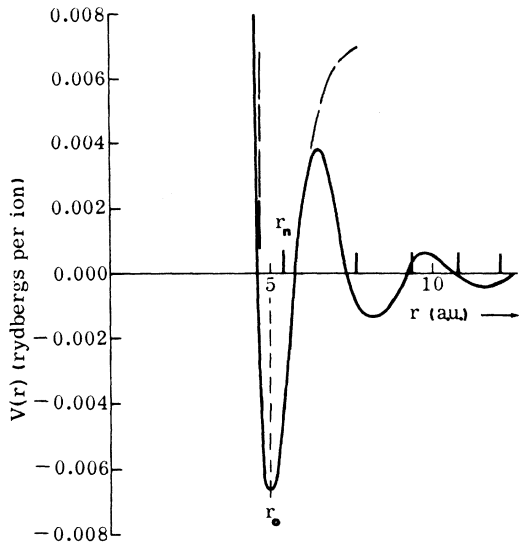

FIG. 2. The interatomic pair pseudopotential as reported by Harrison (Ref. 6) (solid line) and the effective Morse potential calculated in this work (broken line) for aluminum. The zero of energy of the Morse potential was adjusted to coincide with that of the pseudopotential as explained in the text. The vertical bars indicate the relative positions of successive neighbors in the crystal. The displacement between r_0 and r_n for the Morse potential is for 300 °K.

aluminum, it can be seen that the behavior of the pseudopotential is such that the actual magnitude of the potential at lattice sites beyond the nearest neighbors is negligibly small, but because of its oscillatory behavior, the same is not true of its first two derivatives. These give nontrivial contributions to the shear moduli which, while representing only a small fraction of their total magnitude, can account for a large fraction of their percent change with temperature. Consequently, a nearest-neighbor theory based on the Morse potential generally cannot give a quantitatively accurate description of both shear moduli with only three parameters.

A second problem arises from the details of the functional form of the Morse potential. Although this potential may have a very similar overall shape to the actual pseudopotential, the first two derivatives at the nearest neighbor can be quite different. Aluminum is the only fcc metal examined in which the potential minimum lies inside the nearest neighbor, and because the derivatives beyond the potential minimum are not very large, there is only a 30% difference between the values of Dar_n obtained from the shear moduli on the one hand and the thermal-expansion data on the other. However, in all of the other fcc metals considered, the potential minimum lies outside the nearest neighbor, and the derivatives of the potential must be evaluated on its backside, which in the case of the Morse potential is very steep. The actual pseudopotential is not generally as steep in this region, particularly when the potential minimum is outside the nearest neighbor, since it does not have to provide the major contribution to the atomic repulsions that provide crystalline stability. It is easy to determine that the first two derivatives of the Morse potential are both proportional to D, and that it is the value of this quantity that is sacrificed when the derivatives of the Morse potential are too large compared to the actual pseudopotential.

In the fcc metals other than aluminum, the values of D which are deduced from the elastic moduli measurements are about one to two orders of magnitude too small. This is because the backside of the Morse potential is so steep at the nearest neighbors in these cases that the values of D must be made unrealistically small so that the derivatives can be made to correspond to the observed values of the shear moduli. Because of this, it became evident that more realistic values of D could be obtained from the thermal expansion data, since this is primarily dependent upon the overall shape of the potential curve rather than on its derivatives at a particular point. Using Eqs. (15)-(18), values of D as well as ar_n and x can then be easily obtained by computing Γ and Γ' from the values of Dar_n obtained from the thermal expansion data, and then determining values of ar_n and x which best correspond to the observed thermal changes in the shear moduli. The values of D obtained in this way are not consistent with the magnitudes of the shear moduli observed experimentally, but they are consistent with the thermal expansion data and with the overall shape of the potential-energy curve.

The question of the best representation of the experimental data by the theoretical relations is somewhat arbitrary, but in the fcc metals, this was taken to be that representation which averages the deviations between the theoretical and experimental curves equally for the two shear moduli. Figure 3 illustrates the agreement between theory and experiment for aluminum obtained in this way. This agreement is fairly typical of that found for the other fcc metals. The parameters calculated for the Morse potential are not very sensitive to the way in which the comprimise fit between theory and experiment is achieved. In the case of the bcc metals, C' is dependent only on the first derivative of the potential at r_n and this is extremely sensitive to the position of the potential minimum. Moreover, in the bcc case, the next nearest neighbors are only a little beyond the nearest-neighbor distance. Consequently, the the-

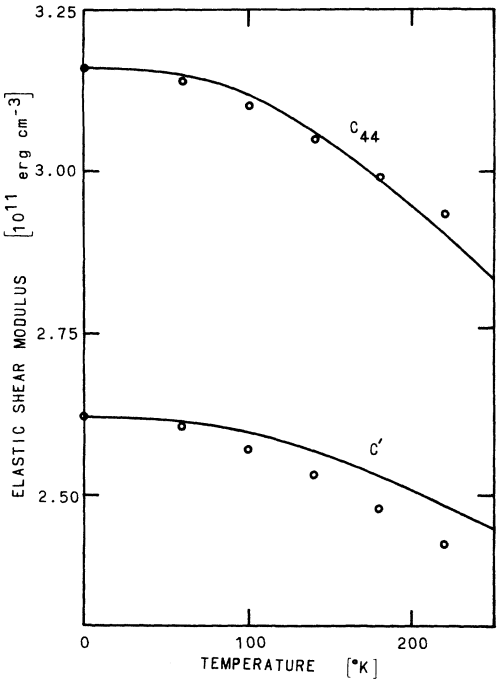

FIG. 3. Calculated (solid lines) and observed variation of the elastic shear moduli of aluminum.

oretical formulas (11) and (18) are probably the least accurate of all. Because of this, the parameters of the Morse potential were determined by Eq. (17) alone in the case of the bcc metals.

Table I illustrates the results of these calculations for various cubic metals. The metals chosen were those for which good elastic moduli data are available including aluminum,[12] silver,[13] gold,[13] lead,[14] copper,[15] and thorium,[16] among the fcc metals, and tungsten,[17] iron,[18] vanadium,[19] potassium,[20] and sodium,[21] among the bcc metals. The Debye temperatures used in the calculations and listed in Table I were obtained from extrapolations of the elastic moduli data to 0°K, except in the cases of sodium and potassium, where they were obtained from low-temperature specific-heat data. The Morse potential parameters listed in the table are fairly realistic representations of the effective behavior of the pseudopotential in the vicinity of the potential minimum in these crystals with respect to their thermal properties, but this representation must be carefully interpreted. The reason for this can be seen by referring back to Fig. 2. The Morse potential does not have any bound states for positive energy values, but this is not generally true for the pseudopotential. In the case of aluminum, the potential barrier extends significantly into the region of positive energies and because of this, a comparison with an effective Morse potential requires that their zeros of energy be adjusted accordingly.

TABLE I. Calculated parameters of the effective Morse potential for various metallic elements.

Metal	Structure	Θ_D (°K)	D (eV)	ar_n	x
Aluminum	fcc	430.3	0.19	8.8	0.063
Copper	fcc	340.1	0.55	4.5	−0.149
Gold	fcc	162.2	0.71	4.4	−0.102
Lead	fcc	105.3	0.35	4.4	−0.228
Silver	fcc	227.4	0.49	4.6	−0.126
Thorium	fcc	165.3	0.87	4.7	−0.201
Iron	bcc	477	0.53	6.0	0.073
Potassium	bcc	91	0.13	5.2	0.035
Sodium	bcc	158	0.13	5.4	0.032
Tungsten	bcc	384.3	1.43	6.1	0.102
Vanadium	bcc	399.3	0.61	7.8	0.072

In Fig. 2, this was accomplished by setting the energies at which the potential minima occur so that they are equal. When this is done, it can be seen that the shapes of the two curves are very similar as are their relative positions with respect to r_n. Thus, the interpretation of the thermal properties in terms of an effective Morse potential must include the recognition that it may have very different properties with respect to its overall shape away from the minimum of energy and its placement on the energy scale from that of the actual pseudopotential.

V. SUMMARY AND CONCLUSIONS

We have presented a theoretical model for the thermal behavior of the elastic shear moduli and the thermal expansion of the cubic metals in terms of the known quantum-mechanical solutions of the Morse potential. This model appears to be most successful when it is dependent only upon the overall shape of the interatomic potential, as is the case in the thermal expansion, and least successful when it depends upon the fine details of the potential, such as the derivatives at r_n which are needed to calculate the elastic shear moduli. Although the actual quantitative calculations are dependent upon the specific solutions for the Morse potential, the success of the model in describing the thermal expansion and the large temperature variation of the shear moduli strongly suggests that the mechanism which it employs is basically correct and not dependent upon the specific assumed form of the interatomic potential in the region of thermal importance.

This mechanism, which is based upon the pseudoatom model of rigid, spherical atomic constituents, starts with an interatomic potential which is independent of density and thus temperature as well. The thermal expansion arises solely from

the anharmonicity of the interatomic potential and the most pronounced thermal effect is the movement of the nearest neighbors with respect to the potential minimum. This thermal effect in turn gives rise to the large variation with temperature of the elastic shear moduli, as observed experimentally. Thus, the thermal properties of these metals are related to a specific microscopic model of the interatomic potential.

APPENDIX: CALCULATION OF THE AVERAGE DISPLACEMENT FOR THE BOUND STATES OF THE MORSE POTENTIAL

The calculation of the diagonal and off-diagonal matrix elements of the radius for the wave functions of the bound states of the Morse potential were completed long ago by Scholz[22] by the use of generating functions. The diagonal matrix elements for a quantum number m which give the quantum-mechanical average for the displacement are given by

$$\langle r_m \rangle = r_0 + a^{-1}[\ln t - \Psi(t-(2m+1))]\,, \tag{19}$$

where $t = 4D/\hbar\omega$, and $\Psi(z)$ is the psi or digamma function defined as the logarithmic derivative of the gamma function.[23] The result (19) is not particularly useful for our purposes since it is not in a form amenable to the direct summations and integrations which we must perform. As discussed earlier, by means of the Taylor-series expansion and perturbation theory, one can demonstrate that in the limit of small anharmonicity, the displacement is proportional to the frequency and the principal quantum number. It is such an expression that we wish to obtain now for small quantum numbers. Noting that t in (19) is a large number, we examine the asymptotic form of $\Psi(z)$,[23]

$$\Psi(z) = \ln(z) - 1/2z - 1/12z^2 + \cdots\,. \tag{20}$$

The expansion (20) does not converge even on the real axis for small values of the argument, but interestingly enough, one can determine by direct calculation that the first three terms in the expansion do give an accurate result on the real axis for values as small as $z = 1$. Since t is a real number, what this means is that the linear approximation (first two terms) is an accurate representation of (19) for a fairly wide range of quantum numbers, and that the addition of the quadratic contribution (first three terms) is quite accurate for virtually all the quantum numbers in the special case of the Morse potential. Since we are interested only in the linear approximation, we will use only the first two terms in (20).

We begin by examining the case $m = 0$. Making use of the recurrence relation[23]

$$\Psi(t+1) = \Psi(t) + t^{-1} \tag{21}$$

one obtains the result

$$\langle r_0 \rangle = a^{-1}\{\ln(t) - (\Psi(t) - (t-1)^{-1})\} + r_0\,. \tag{22}$$

Now using the first two terms in the expansion (20), one gets

$$\begin{aligned}\langle r_0 \rangle - r_0 &= a^{-1}[(2t)^{-1} + (t-1)^{-1}] + O(t^{-2}) \\ &= \tfrac{3}{2}(at)^{-1} + O(t^{-2})\,.\end{aligned} \tag{23}$$

Next, by repeated use of (21), as well as (20), one obtains for the case $m = 1$

$$\begin{aligned}\langle r_1 \rangle &= a^{-1}[\ln(t) - \Psi(t-3)]\,, \\ &= \langle r_0 \rangle + a^{-1}[(t-2)^{-1} + (t-3)^{-1}] \\ &= \langle r_0 \rangle + 2(at)^{-1} + O(t^{-2})\,.\end{aligned}$$

This process can be repeated over and over agian, and by induction, one obtains for the general case of the quantum number m the result

$$\begin{aligned}\langle r_m \rangle &= \langle r_0 \rangle + 2m(at)^{-1} + O(t^{-2})\,, \\ &= r_0 + 2(at)^{-1}(m + \tfrac{3}{4}) + O(t^{-2})\,,\end{aligned} \tag{24}$$

which is the desired result.

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