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Calculated thermal properties of metals

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The thermal properties of the 14 nonmagnetic cubic metals through the 4*d* transition series are derived from first-principles electronic-structure calculations coupled with a Debye treatment of the vibrating lattice. Debye temperatures and Grüneisen constants are derived from an analysis of the compressional characteristics of rigid-lattice binding curves and are used to define the contribution of the lattice vibrations to the free energy. A minimization of the resulting free energy with respect to volume yields temperature-dependent lattice separations and coefficients of thermal expansion. Theoretical values of cohesive energies, equilibrium lattice separations, bulk moduli, Debye temperatures, Grüneisen constants, and coefficients of thermal expansion are derived directly from computed electronic-structure results. Good agreement with experiment is found for all computed quantities.

INTRODUCTION

Using self-consistent band calculations, it now is a routine matter to calculate the binding curves for a system of atoms on a given lattice. Analysis of such curves for elements[1] and for simple compounds and alloys yields theoretical ground-state properties such as cohesive energies, equilibrium lattice separations, and bulk moduli that are in good agreement with experiment. In addition, binding curves displayed over an extended volume range show an anharmonic character and slant towards higher volumes, thus implying thermal expansion and vibrations of atoms from their mean lattice positions. In this work we use Debye-Grüneisen theory to extend the analysis of calculated binding curves to finite temperatures. In addition to the usual ground-state properties, we derive a characteristic Debye temperature from the calculated bulk modulus, and a Grüneisen constant from the anharmonicity of the binding curve. The evaluation of these two quantities is sufficient to define the free and zero-point energies of a vibrating Debye lattice, which we then add to the calculated binding curves to yield free energies.

We have done a series of electronic-structure calculations using the augmented-spherical-wave method and the local-density-functional theory[2] for the 14 nonmagnetic fcc and bcc elemental metals up to silver with Wigner-Seitz radii spanning the range of approximately ±10% of the equilibrium ground-state lattice separation, r_0, in intervals of 0.02 a.u. The computation of ground-state and thermal properties requires the evaluation of various derivatives and is most easily accomplished by

TABLE I. Morse parameters for the cubic metals on a rigid lattice. The equilibrium Wigner-Seitz radius, r_0, is in atomic units (a.u.), and λ is in reciprocal atomic units (a.u.$^{-1}$). The linear parameters D and A are in Ry/atom. E_{atom} is the calculated free-atom energy in Ry.

System	r_0 (a.u.)	λ (a.u.$^{-1}$)	D	A	E_{atom}
bcc Li	3.1429	0.7339	0.1150	−14.719	−14.709
bcc Na	3.7950	0.7269	0.0872	−322.900	−322.902
fcc Al	2.9594	1.2142	0.2163	−482.715	−482.637
bcc K	4.7719	0.6303	0.0724	−1196.377	−1196.382
fcc Ca	4.0186	0.6095	0.2728	−1351.321	−1351.442
bcc V	2.8246	0.9953	0.6889	−1883.254	−1883.529
fcc Cu	2.6658	1.5099	0.2481	−3275.512	−3275.464
bcc Rb	5.1530	0.5898	0.0696	−5872.465	−5872.477
fcc Sr	4.3813	0.6276	0.2167	−6258.609	−6258.683
bcc Nb	3.1359	0.8634	0.9270	−7501.952	−7502.361
bcc Mo	2.9972	1.0732	0.8502	−7945.705	−7946.087
fcc Rh	2.8627	1.4945	0.4319	−9366.435	−9366.418
fcc Pd	2.9281	1.5784	0.2727	−9870.423	−9870.419
fcc Ag	3.0541	1.5788	0.1713	−10 389.980	−10 389.748

TABLE II. Comparison of Morse parameters for some cubic metals. The Slater values are derived from experimental latent heats of vaporization and compressibilities.

	D (Ry)		λ (a.u.$^{-1}$)	
System	Slater	Theory	Slater	Theory
bcc Li	0.1148	0.1150	0.84	0.7339
bcc Na	0.0835	0.0872	0.72	0.7269
fcc Al	0.2155	0.2163	1.28	1.2142
bcc K	0.0698	0.0724	0.46	0.6303
fcc Ca	0.1365	0.2728	0.88	0.6095
fcc Cu	0.2605	0.2481	1.50	1.5099
bcc Rb	0.0657	0.0696	0.50	0.5898
bcc Mo	0.4974	0.8502	1.68	1.0732
fcc Ag	0.0861	0.1713	1.48	1.5788

fitting the calculated points to a functional form. We have found that a fit to the four-parameter Morse function defined in Eq. (A12) of the Appendix yields an adequate representation of our calculations. The four Morse parameters, A, D, λ, and r_0 defined in the Appendix are summarized in Table I. In all cases, the fit to the functional form reproduces the calculated energies to better than a few tenths of a mRy over the specified range. Included for reference are the calculated free-atom total energies.

Slater[3] attempted to construct effective Morse curves by identifying D with the experimental cohesive energy, computing r_0 from the experimental density, and extracting λ from the experimental compressibility. In Table II we compare our theoretical values of D and λ with Slater's experimentally derived values for a number of systems studied. We note that D values are in agreement except for calcium, molybdenum, and silver. λ values (note that Slater's r's are interatomic separations rather than Wigner-Seitz radii), which are crucial in defining the volume dependence of the energy are also in reasonable agreement except for calcium and molybdenum.

Recently, it has been discovered[4] that binding curves can be scaled such that all metals obey a universal function involving a single exponential. For a given metal, this universal function is usually characterized by a number of parameters obtained from experimental data. An extension[5] of the universal function yields a universal equation of state which can predict thermal properties from experimental parameters obtained at a single temperature. The analysis, which includes consideration of the vibration of atoms from their equilibrium positions, yields coefficients of thermal expansion which are in good agreement with experiment at temperatures above the Debye temperature. Our present work, based on a fit to Morse functions, also demonstrates that thermal properties of simple systems can be predicted from data appropriate to a single temperature (ground state, zero temperature). Our present work, however, goes beyond the earlier work, and extracts the entire thermal dependence of the coefficient of thermal expansion from calculated (as opposed to experimentally determined) binding curves.

The work that follows can be conveniently divided into three sections, the first dealing with the determination of an effective Debye temperature from the calculated bulk modulus, the second dealing with the calculation of the Grüneisen constant from higher derivatives of the binding curves, and the third dealing with the calculated free energy of the system and its implications. In the first section we define a Debye average to replace the usual longitudinal and transverse modes of a vibrating system, and find a relation between the Debye temperature and the bulk modulus. We show that we can define a Debye average by assuming that the longitudinal modulus (obtained from longitudinal sound velocity), and the shear modulus (obtained from transverse sound velocity) are both proportional to the bulk modulus. In the second section, we show that the Grüneisen constant is related to higher derivatives of the binding curves, and present an argument for a particular expression which we believe to be applicable at low temperatures. In the third section we use calculated Debye temperatures and Grüneisen constants to find the free energy of the system as a function of both volume and temperature and compute temperature-dependent lattice separations and coefficients of thermal expansion. Finally, we compare our calculated ground-state and thermal properties with experiment.

DEBYE TEMPERATURE

If we assume that lattice vibrations can be accounted for by the Debye theory, the lattice can vibrate at all frequencies up to a Debye cutoff frequency, ω_D, defined by

$$\frac{h}{2\pi}\omega_D = k_B\Theta_D \ , \tag{1}$$

where h and k_B are Plank's and Boltzmann's constants, and Θ_D is the characteristic Debye temperature. Assuming a constant sound velocity, v, given by

$$v = \left[\frac{B}{\rho}\right]^{1/2} , \tag{2}$$

where B is the bulk modulus defined in the Appendix, and ρ is the density, it can be shown that

$$\Theta_D = (6\pi^2)^{1/3}\frac{h}{2\pi k_B}\left[\frac{4\pi}{3}\right]^{1/6}\left[\frac{rB}{M}\right]^{1/2} , \tag{3}$$

where M is the atomic weight. With B in kbar and r in a.u., the Debye temperature (in K) becomes

$$\Theta_D = 67.48 \left[\frac{rB}{M} \right]^{1/2} . \tag{4}$$

The use of this expression to evaluate $(\Theta_D)_0$ at $r = r_0$ (i.e., at the rigid-lattice equilibrium separation), using the calculated (or experimental) bulk modulus yields Debye temperatures much larger than the experimental values. In practice, this expression must be multiplied by an empirical constant[6] obtained from experimental data. The difficulty arises from the assumption that the speed of sound is proportional to $\sqrt{B}$. Even with an isotropic medium assumption, the sound velocities associated with the transverse (shear) and longitudinal modes are related to the elastic constants of the system in a complicated manner.[7,8] Anderson[9] expresses the low-temperature average for the sound velocity for an isotropic crystal (i.e., isotropic transverse and longitudinal sound velocity) as

$$v = \left[\frac{1}{3} \left[\frac{2}{v_t^3} + \frac{1}{v_l^3} \right] \right]^{-1/3} , \tag{5}$$

where $v_t = \sqrt{S/\rho}$ and $v_l = \sqrt{L/\rho}$; S and L being the shear and longitudinal moduli, respectively. Thus v can be directly related to S and L. In addition, Anderson's work shows that, for the nonmagnetic cubic elements considered here, $L \simeq 1.42B$ (this is equivalent to the observation that, for these elements, Poisson's ratio is approximately constant and approximately equal to $\frac{1}{3}$), and $S \simeq 0.30B$. The extent to which these relations are valid for a number of different elements is shown in Figs. 1 and 2, where it is seen that only molybdenum is not well represented by these relations. Note that the constants of proportionality are non-system-specific (the same constants can be used for all systems considered). Using these relations and Anderson's definition, we can express the average sound velocity in terms of the bulk modulus as

$$v = 0.617 \left[\frac{B}{\rho} \right]^{1/2} . \tag{6}$$

Thus the previous expression for Θ_D must be modified by a scaling factor of 0.617. With these considerations, we can now proceed to evaluate Θ_D using only theoretical quantities derived from our fit to first-principles energy-band results. Evaluated at $r = r_0$, this Debye temperature is labeled $(\Theta_D)_0$. Including the scaling factor (and specifying r in a.u. and B in kbar), we find

$$(\Theta_D)_0 = 41.63 \left[\frac{r_0 B}{M} \right]^{1/2} , \tag{7}$$

where B is the bulk modulus evaluated at r_0.

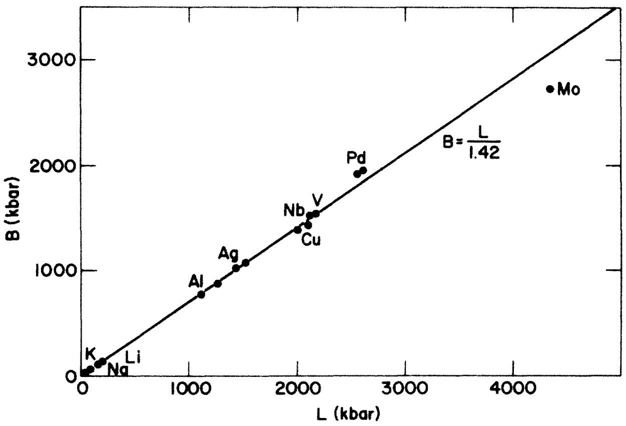

FIG. 1. Longitudinal vs bulk modulus derived from an analysis (Ref. 9) of experimental data for the nonmagnetic cubic elements considered in the present work. Lithium, aluminum, copper, palladium, and silver are represented by two points indicating the spread between low-temperature and room-temperature experimental values.

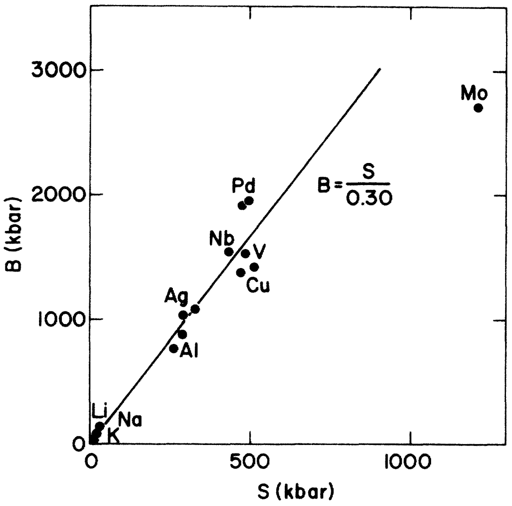

FIG. 2. Shear vs bulk modulus derived from an analysis (Ref. 9) of experimental data for the nonmagnetic cubic elements considered in the present work. Lithium, aluminum, copper, palladium, and silver are represented by two points indicating the spread between low-temperature and room-temperature experimental values.

GRÜNEISEN CONSTANT

Anharmonic effects in the vibrating lattice are usually described in terms of a Grüneisen constant, γ, which can be defined as

$$\gamma = -\frac{\partial \ln \Theta_D}{\partial \ln V} , \tag{8}$$

and which gives the volume dependence of Θ_D. Using the theoretical expression for Θ_D, we find that

$$\gamma = -\frac{1}{6} - \frac{1}{2} \frac{\partial \ln B}{\partial \ln V} . \tag{9}$$

But, from the definition of the bulk modulus given in the Appendix,

$$\frac{\partial \ln B}{\partial \ln B}=1+\frac{\partial^2 P/\partial V^2}{\partial P/\partial V}\ , \tag{10}$$

and

$$\gamma=-\frac{2}{3}-\frac{V}{2}\frac{\partial^2 P/\partial V^2}{\partial P/\partial V}\ . \tag{11}$$

This expression, first derived by Slater,[3] contains the implicit assumption that Poisson's ratio, σ, is constant (independent of volume) and that all vibrational modes are excited.

It should be noted that a constant γ implies a Debye spectrum with frequencies that all vary with volume in the same manner. Vibrations in a real solid, however, are somewhat more complicated. Assuming the same cutoff wavelength for each type of vibration (longitudinal or transverse), it is readily seen that all modes are excited at high temperatures. However, γ is dominated by lower-frequency transverse modes at low temperatures. Slater's expression for γ assumes equal excitation of all modes and is effectively a high-temperature average. This expression for γ is therefore valid at high temperatures and, in general, yields γ values that are larger than values derived from low-temperature specific heat data by an additive factor of about $\frac{1}{3}$. By defining appropriate high- and low-temperature averages, Barron[10] has also shown that

$$\gamma_{\mathrm{HT}}-\gamma_{\mathrm{LT}}\simeq\tfrac{1}{3} \tag{12}$$

for cubic close-packed lattices with central forces between nearest neighbors. That is γ tends to increase with increasing temperature[11,12] (aluminum and perhaps copper seem to be exceptions[13,14]). Since we are interested in comparing calculated Grüneisen constants with values derived from low-temperature specific heat data, we find that

$$\gamma=\gamma_{\mathrm{LT}}=-1-\frac{V}{2}\frac{\partial^2 P/\partial V^2}{\partial P/\partial V}\ . \tag{13}$$

This expression is identical to one proposed by Dugdale and MacDonald,[15] and yields Grüneisen constants in better agreement with low-temperature experimental values than Slater's expression. Accordingly, we use this latter expression to evaluate γ from our theoretical fit to first-principles energy-band results.[16]

In this section we have gone to rather elaborate lengths to justify the use of γ_{LT} in order to facilitate comparison with γ values derived from low-temperature specific heat data. In addition, it is generally found that[10] thermal expansion is less than would be expected from the high-temperature value of γ. Since most of the expansion occurs at relatively low temperatures, we expect that γ_{LT} is more appropriate for determining thermal expansion. These concepts are consistent with negative values of $\partial\sigma/\partial V$ (Ref. 17) and a general increase in γ with increasing temperature. The latter is confirmed theoretically, for an isotropic medium with central forces, by Barron[10] and by Blackman.[11]

Our initial determination of γ is based on rigid-lattice results, and is labeled γ_0. This is considered to be only a first approximation. That is, we evaluate γ_0 using Eq. (13) with $V=V_0$. Using the volume derivatives, $\partial^2 P/\partial V^2$ and $\partial P/\partial V$, evaluated at V_0 from Eq. (A6) of the Appendix, the expression for the Grüneisen constant takes the simple form

TABLE III. Bulk modulus, Debye temperature, and Grüneisen constant derived from a Morse fit of the rigid-lattice energy, E_{el}.

System	B_0 (kbar)	$(\Theta_D)_0$ (K)	γ_0
bcc Li	153.8	347.4	1.153
bcc Na	94.8	164.7	1.379
fcc Al	840.9	399.9	1.797
bcc K	47.1	99.8	1.504
fcc Ca	204.0	188.3	1.245
bcc V	1885.5	425.7	1.406
fcc Cu	1655.7	347.0	2.023
bcc Rb	36.7	61.9	1.520
fcc Sr	152.0	114.8	1.375
bcc Nb	1719.6	317.2	1.354
bcc Mo	2549.6	371.6	1.608
fcc Rh	2629.8	356.1	2.139
fcc Pd	1810.7	293.9	2.311
fcc Ag	1090.7	231.4	2.411

$$\gamma_0=\frac{\lambda r_0}{2} \tag{14}$$

(compare with Ref. 3, p. 452, Eq. 2.5). The computed values of B_0, $(\Theta_D)_0$, and γ_0, for the cubic elements studied, are listed in Table III. The Slater expression for γ would yield our values plus an additive constant of $\frac{1}{3}$.

FREE ENERGY

Free energy, F, of the vibrating system can be expressed as the sum of the total energy of the rigid lattice and the free energy of the vibrating lattice. Since the electronic entropy is expected to be negligible, the free energy can be expressed as

$$F(r,T)=E(r)+E_D(r,T)-TS_D(r,T)\ , \tag{15}$$

where T is temperature and E_D and S_D are Debye functions, with

$$E_D(r,T)-E_0=3k_BTD(\Theta_D/T)\ , \tag{16}$$

and

$$S_D(r,T)=3k_B[\tfrac{4}{3}D(\Theta_D/T)-\ln(1-e^{-\Theta_D/T})]\ . \tag{17}$$

The Debye function $D(\Theta_D/T)$ varies from unity at high temperatures to zero at low temperatures, and is readily available in tabulated form.[18] Here, E_0 is the zero-point energy which, within the Debye approximation, can be expressed as

$$E_0=\tfrac{9}{8}k_B\Theta_D\ . \tag{18}$$

The final expression for the free energy is

$$F(r,T)=E_{\mathrm{el}}(r)-k_BT[D(\Theta_D/T)+3\ln(1-e^{-\Theta_D/T})]+\tfrac{9}{8}k_B\Theta_D\ . \tag{19}$$

Here, the r dependence enters by way of Θ_D through the relation

$$\Theta_D/(\Theta_D)_0=(V_0/V)^\gamma=(r_0/r)^{3\gamma} . \qquad (20)$$

Thus we have expressed the free energy of the vibrating system in terms of theoretical quantities derived from a fit to electronic-structure calculations involving the atomic number as the only input. Subsequent Morse fits at finite-temperature intervals yields, directly, values of $r_0(T)$. Finally, the coefficient of thermal expansion $\alpha(T)$ is

$$\alpha(T)=\frac{1}{r_0}\frac{dr_0}{dT} . \qquad (21)$$

In addition to $r_0(T)$ and $\alpha(T)$, our analysis also yields $B_0(T)$, $(\Theta_D)_0(T)$, and $\gamma_0(T)$; the latter showing relatively weak temperature dependences except for the softer alkali metals.

As an example, we show the details of our analysis for the case of potassium, an element with large coefficients of thermal expansion, and correspondingly large temperature variation of equilibrium Wigner-Seitz radius, bulk modulus, Debye temperature, and Grüneisen constant. In Fig. 3 we show calculated free-energy curves for this system at 100 K intervals over a limited range of r values. For reference, we have also included the total energy for the rigid lattice. Note that, as a consequence of the zero-point energy, the free-energy curve for 0 K is higher than the rigid-lattice energy. As the temperature increases, the free energy becomes more negative because of the entropy of vibration. The lattice expansion is readily seen from the positions of the minima (obtained from a Morse analysis) in the free-energy curves.

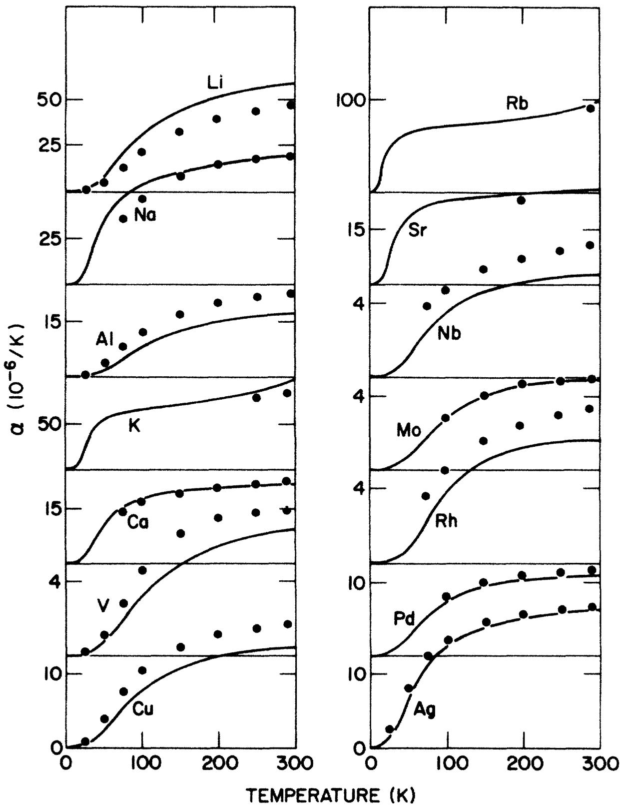

FIG. 4. Calculated coefficient of thermal expansion vs temperature for the nonmagnetic cubic elements considered, along with some experimental (Ref. 19) points.

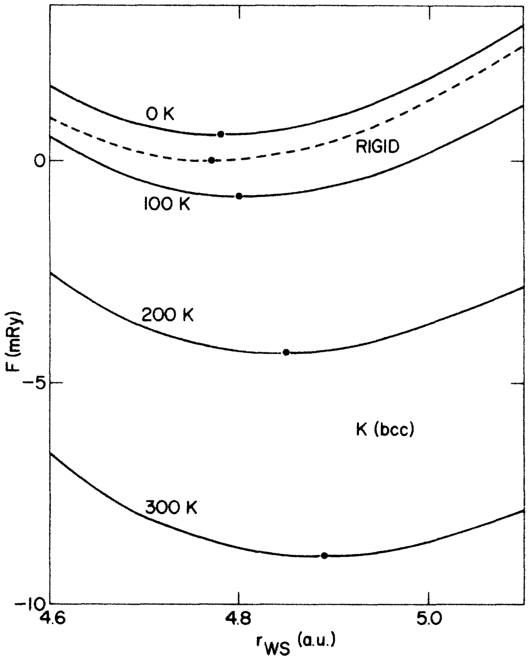

FIG. 3. Calculated free-energy curves for potassium at a number of temperatures. The dashed curve is the rigid-lattice energy. The free energy is relative to the rigid-lattice minimum. The positions of the minima are obtained from a Morse analysis (see text).

In Fig. 4 we show the calculated coefficients of thermal expansion, along with experimental data[19] for all of the elements considered. Note that the α scale differs for different elements, being an order of magnitude greater for the "soft" alkali metals compared with the "hard" midtransition metals. In general, the agreement with experiment is excellent. It should be noted that the calculated Debye temperatures determine the position of the "knee," and that the calculated Grüneisen constants determine the high-temperature "amplitude" of the curves. Thus these results would indicate that the theoretical γ is too high for lithium and strontium, and too low for aluminum, vanadium, copper, and niobium. In addition, the calculated Θ_D would seem to be too low for sodium.

COMPARISON WITH EXPERIMENT

As discussed above, a Morse fit to the temperature-dependent free energy yields temperature dependent r_0 and α values, along with B_0 and $(\Theta_D)_0$ values which show weak temperature dependences. Table IV shows our theoretical results. Here, the cohesive energy is found by forming

$$E_{\mathrm{coh}}=(E-E_0)_{r=r_0}-E_{\mathrm{atom}} , \qquad (22)$$

TABLE IV. Theoretical cohesive energies (E_{coh}), equilibrium Wigner-Seitz radii (r_0), bulk moduli (B_0), Grüneisen constants (γ_0), Debye temperatures [$(\Theta_D)_0$], and room-temperature coefficients of thermal expansion (α).

System	E_{coh} (Ry)	r_0 (a.u.)	B_0 (kbar)	γ_0	$(\Theta_D)_0$ (K)	α (10^{-6}/K)
bcc Li	0.122	3.196	136.7	1.16	345.0	58.7
bcc Na	0.084	3.868	80.6	1.39	164.0	70.3
fcc Al	0.292	2.975	791.5	1.80	398.0	17.3
bcc K	0.066	4.781[a]	37.9	1.51	99.4	91.0
fcc Ca	0.160	4.043	194.8	1.23	188.0	21.2
bcc V	0.411	2.831	1852.0	1.41	425.0	6.8
fcc Cu	0.294	2.677	1573.0	2.02	346.0	13.4
bcc Rb	0.057	5.159[a]	29.2	1.52	61.8	95.7
fcc Sr	0.142	4.413	143.0	1.38	114.6	24.6[b]
bcc Nb	0.515	3.141	1697.0	1.35	317.0	5.4
bcc Mo	0.465	3.002	2513.0	1.61	371.0	4.9
fcc Rh	0.446	2.869	2556.0	2.14	355.0	6.5
fcc Pd	0.275	2.938	1726.0	2.31	293.0	10.8
fcc Ag	0.224	3.070	1007.0	2.41	231.0	18.8

[a] 5 K.

[b] 200 K.

where E_0 is the zero-point energy calculated from theoretical Debye temperatures and Grüneisen constants, and E_{atom} is the free-atom energy (including spin polarization). The Wigner-Seitz radii, r_0, are evaluated at room temperature, except for potassium and rubidium where low-temperature values are available for comparison. In all cases, the bulk modulus, B_0, is determined at room temperature (the room-temperature value can be as much as 20% less than the low-temperature value, especially for alkali metals like potassium and rubidium). The Grüneisen constants show a weak increase with temperature, the tabulated values being appropriate for low temperatures (because the experimental values to be used for comparison are derived from low-temperature specific heat data). Low-temperature Debye temperature values are tabulated (again, because the experimental values used for comparison are derived from low-temperature specific heat data). The coefficients of thermal expansion, α, are room-temperature values, except for strontium which is at 200 K for reasons of experimental comparison. Table V is the experimental analog of Table IV. The experimental Wigner-Seitz radii were computed from experimental lattice constants at room temperature for all elements except potassium and rubidium where low-temperature (5 K) values were used.[20] The coefficients of thermal expansion[19] are room-temperature values except for strontium which is at 200 K. Bulk moduli, Grüneisen constants, and Debye temperatures are from Gschneider's review article[21] with the latter two quantities being derived from low-temperature specific heat data.

The sensitivity of the analysis on the expression used

TABLE V. Experimental cohesive energies (E_{coh}), equilibrium Wigner-Seitz radii (r_0), bulk moduli (B_0), Grüneisen constants (γ_0), Debye temperatures [$(\Theta_D)_0$], and room-temperature coefficients of thermal expansion (α).

System	E_{coh} (Ry)	r_0 (a.u.)	B_0 (kbar)	γ_0	$(\Theta_D)_0$ (K)	α (10^{-6}/K)
bcc Li	0.122	3.265	115.7	0.91	352.0	46.6
bcc Na	0.083	3.992	68.1	1.33	157.0	69.0
fcc Al	0.245	2.991	721.6	2.18	423.0	23.0
bcc K	0.069	4.862[a]	31.8	1.37	89.4	82.0
fcc Ca	0.134	4.123	152.0	1.07	234.0	22.1
bcc V	0.389	2.818	1619.0	1.55	326.0	7.8
fcc Cu	0.258	2.670	1309.0	1.97	342.0	16.7
bcc Rb	0.064	5.197[a]	31.4	1.85	54.0	91.0
fcc Sr	0.125	4.436	116.1	0.95	147.0	23.0[b]
bcc Nb	0.556	3.071	1702.0	1.74	241.0	7.1
bcc Mo	0.501	2.928	2725.0	1.65	459.0	5.0
fcc Rh	0.424	2.809	2705.0	2.43	480.0	8.2
fcc Pd	0.287	2.873	1808.0	2.47	283.0	11.6
fcc Ag	0.218	3.018	1007.0	2.46	228.0	19.0

[a] 5 K.

[b] 200 K.

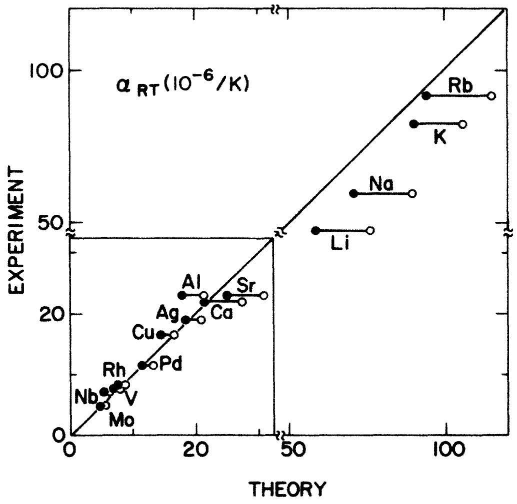

FIG. 5. Comparison of theoretical and experimental coefficients of thermal expansion at room temperature α_{RT} for the nonmagnetic cubic elements (the calcium values are taken at 200 K). Solid points represent calculations based on the Dugdale and MacDonald (Ref. 15) expression for γ, and open points correspond to calculations based on the Slater (Ref. 3) expression for γ.

to calculate γ is shown in Fig. 5 where we compare theoretical and experimental coefficients of thermal expansion evaluated at room temperature, α_{RT} (the calcium value is taken at 200 K). Perfect agreement is represented by the 45° line. The solid points were calculated using Eq. (13) and are in agreement with Fig. 4 and Table IV, while the open points were evaluated using Slater's expression given in Eq. (11). Note the change in scale separating the alkaline metals. The better overall agreement between theory and experiment using Eq. (13) is obvious.

In addition to temperature-dependent Wigner-Seitz radii, the Morse analysis described in the Appendix also yields temperature-dependent bulk moduli. With increasing temperature, the decrease in bulk moduli scales roughly with the thermal expansion and is largest for the softer alkali metals. Recent experimental studies[22] on the latter provide a test of our analysis. In Fig. 6 we compare our calculated temperature dependence of the reduced equilibrium radii, $r_0/[r_0(T=0)]$ (evaluated at zero pressure), with experiment for bcc lithium, sodium, potassium, and rubidium. Similarly, our calculated temperature dependence of the reduced bulk moduli, $B_0/[B_0(T=0)]$ (evaluated at zero pressure) is compared with experiment in Fig. 7. Both comparisons are excellent and indicate that our analysis yields reasonably correct temperature variations of Wigner-Seitz radii and bulk moduli. Thus our first-principles calculations, with atomic numbers as the only input, yield quantities in reasonable agreement with experiment. The results show that our determination of Debye temperatures and Grüneisen constants, which are of fundamental importance in the analysis, is qualitatively correct.

The alkali metals, especially potassium and rubidium, are characterized by low cohesive energies, bulk moduli, and Debye temperatures, and by high coefficients of thermal expansion. These properties, in turn, imply low melting temperatures. The Debye theory is basically a harmonic theory of lattice vibrations. It makes drastic simplifying assumptions and is therefore not expected to be valid near the melting point. In our analysis, however, we recompute Debye temperatures and Grüneisen constants at each temperature. Our treatment is therefore quasiharmonic because we allow the system to expand and apply a harmonic theory at each stage (temperature) of the expansion. The effect of this quasiharmonic treatment is most apparent in our calculated $\alpha(T)$ curves shown in Fig. 4. For potassium and rubidium, the high-temperature regions deviate from a linear behavior, and are concave upwards. Experimentally, the coefficient of thermal expansion tends to diverge as the temperature approaches the melting point. Our calculated behavior for potassium and rubidium indicates a precursor to the melting point, which is just above room temperature for these two elements. Thus our

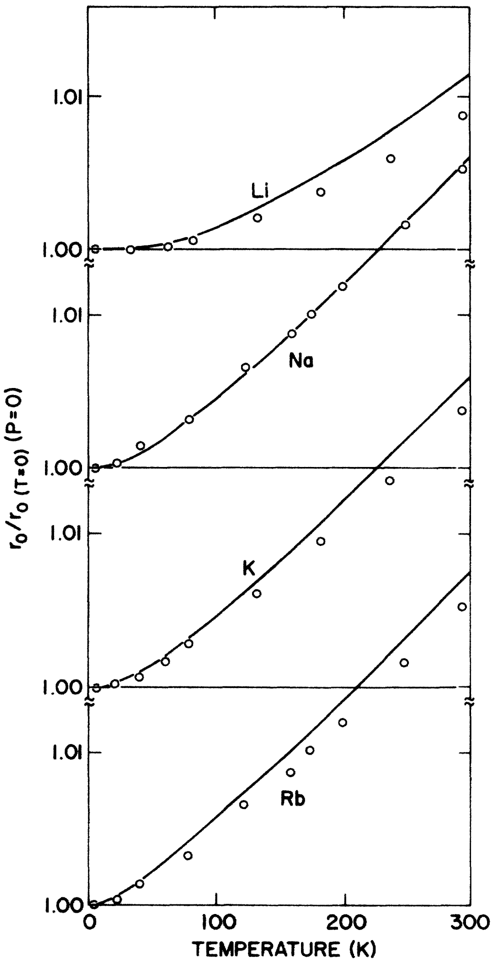

FIG. 6. Comparison of the theoretical and experimental temperature dependence of the ratio of the Wigner-Seitz radius to the zero-temperature value (evaluated at zero pressure) for the alkali metals. The points represent experimental values taken from Ref. 22.

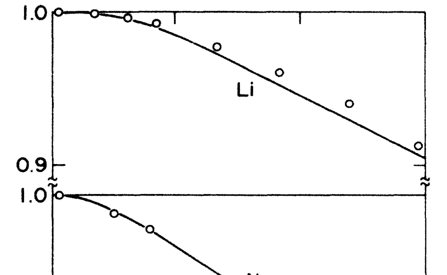

FIG. 7. Comparison of the theoretical and experimental temperature dependence of the ratio of the bulk modulus to the zero-temperature value (evaluated at zero pressure) for the alkali metals. The points represent experimental values taken from Ref. 22.

electronic-structure calculations, coupled with our quasiharmonic treatment of the vibrating lattice, lead to a qualitatively accurate model which even captures the behavior of systems just below the melting point.

SUMMARY

In the foregoing analysis of the nonmagnetic cubic elements the system is allowed to expand under thermal excitation. At each stage of expansion, the Debye theory, based on a harmonic approximation, is used to treat the lattice vibrations. We begin with binding curves for nonvibrating nuclei and their associated electrons, and use a Morse analysis to evaluate a Debye temperature and a Grüneisen constant from the bulk modulus and pressure derivatives of the binding curve. We find that, in order to evaluate Debye temperatures consistent with experiment it is necessary to use experimentally observed relations between the bulk modulus and the longitudinal and shear moduli which lead to a scaling factor of 0.617 if the speed of sound is expressed as a square root of the bulk modulus divided by the density. We also find that the Slater expression yields Grüneisen constants which are usually larger than experiment by an additive constant of about $\frac{1}{3}$ and accordingly use Eq. (13) to find γ. With these prescriptions for evaluating the Debye temperature and the Grüneisen constant, we express the free energy of the vibrating lattice as a function of both volume (r) and temperature. A Morse analysis of the resulting free-energy curves yields the equilibrium volume (r_0) and bulk modulus as functions of temperature, and the temperature derivative of the former leads directly to coefficients of thermal expansion versus temperature.

We have shown that the compressional characteristics of rigid-lattice binding curves contain sufficient information to define parameters which lead to an approximate and useful definition of the free energy of the cubic nonmagnetic elements considered. Based on this work, we can conclude that a bulk modulus calculated with a scaling factor of 0.617 can be used to compute reasonable values of the Debye temperature. We found that γ values derived from Eq. (13) yield coefficients of thermal expansion in better overall agreement with experiment than γ values obtained from Slater's expression, especially for the alkaline metals.

The underlying rigid-lattice energy-band calculations yield a first approximation to the basic parameters, Θ_D and γ, used in the thermal analysis. The calculations, which are self-consistent and are based on the augmented-spherical-wave method, utilize the local-density approximation. The work presented here demonstrates that the local-density approximation, which has previously been considered applicable only to ground-state properties, yields binding curves with compressional characteristics which give Debye and Grüneisen parameters capable of defining the free energy of the system as a function of temperature. We have shown that an analysis of the resulting free energy leads to coefficients of thermal expansion in reasonable agreement with experiment. The remarkable success of this analysis is a tribute to the adequacy of the local-density approximation to provide adequately accurate ground-state and thermal properties of materials.

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APPENDIX

To analyze the binding curves derived from our energy-band calculations, we choose to fit to an exponential function of the form,

$$E(r)=a+be^{-\lambda r}+ce^{-2\lambda r}, \tag{A1}$$

where E is the total energy, r is the Wigner-Seitz radius, and λ, a, b, and c are four fitting parameters. The fitting procedure can be simplified by letting

$$x=e^{-\lambda r}\ , \tag{A2}$$

so that

$$E=a+bx+cx^2\ . \tag{A3}$$

The pressure, P, can now be evaluated by taking the negative volume derivative of the total energy. Thus

$$P=-\frac{\partial E}{\partial V}\ , \tag{A4}$$

where the volume, V, is

$$V=\frac{4\pi}{3}r^3\ . \tag{A5}$$

In terms of the variable, x, and the exponential fitting parameters,

$$P=\frac{x\lambda^3}{4\pi(\ln x)^2}(b+2cx)\ . \tag{A6}$$

Since the pressure vanishes at $r=r_0$, where $(b+2cx)=0$ and $x=x_0$,

$$x_0=\frac{-b}{2c}\ , \tag{A7}$$

and

$$r_0=-\frac{\ln x_0}{\lambda}\ . \tag{A8}$$

Here, r_0 can be interpreted as the equilibrium Wigner-Seitz radius for the rigid lattice. In general, this value is less than the corresponding value for the vibrating lattice, even at zero temperature because of the zero-point energy.

The bulk modulus, B, defined as

$$B=-V\frac{\partial P}{\partial V}\ , \tag{A9}$$

then becomes

$$B=-\frac{x\lambda^3}{12\pi\ln x}\left[(b+4cx)-\frac{2}{\ln x}(b+2cx)\right]\ . \tag{A10}$$

However, since $(b+2cx)=0$ at r_0, where $x=x_0$,

$$B(r_0)=-\frac{cx_0^2\lambda^3}{6\pi\ln x_0}\ . \tag{A11}$$

The above expression gives the bulk modulus for the rigid lattice. The bulk modulus for the vibrating lattice will differ slightly from the above, even at zero temperature because of the zero-point energy.

The exponential fit discussed here is mathematically equivalent to a fit to a Morse function of the form,

$$E(r)=A-2De^{-\lambda(r-r_0)}+De^{-2\lambda(r-r_0)}\ . \tag{A12}$$

A Morse fit is operationally more difficult because of the appearance of two nonlinear parameters λ and r_0. It is easily verified that the two fits are equivalent with the fitting parameters related by

$$a=A\ , \tag{A13}$$

$$\frac{b}{c}=-2e^{-\lambda r_0}\ , \tag{A14}$$

and

$$D=\frac{b^2}{4c}\ . \tag{A15}$$

Thus a least-square fit yielding the four parameters A, D, λ, and r_0 completely specifies the calculated binding curves.

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