1. The electrons obey the Lax 2-band model[12]

$$E(1+E/E_g)=\sum_i \hbar^2k_i^2/2m_i \qquad (6)$$

and

$$m_0/m_i=1+2|M_i|^2/E_g\cong 2|M_i|^2/E_g\,, \qquad (7)$$

where M_i is the appropriate momentum matrix element and is independent[5] of x, and m_0 is the free-electron mass. Equations (6) and (7) are probably incorrect in the heavy-mass direction[13,3] and this may lead to small errors.

2. The hole effective masses are independent of x. (Actually the hole density of states effective mass is about 25% larger at $x=0.05$ than in pure bismuth.[14] This effect is unimportant for our purposes.)

To proceed we take the hole masses from Ref. 2 and from the electron masses given there we calculate the matrix elements M_i. Then from $E_g=|L_s-L_a|$ and $E_0=T_{45}^- - \max(L_s,L_a)$ we calculate the electron Fermi energy E_F by equating the number of electrons and holes. The dHvA area and the cyclotron mass ratios are then readily calculated. The latter is given by

$$m^c(x)/m^c(0)=(E_g+2E_F)/(E_g^0+2E_F^0)\,. \qquad (8)$$

These ratios are compared with experiment in Fig. 3; the agreement is good.

The crossing of L_s and L_a at $x\approx 0.06$ is an essential part of this model. It should be easy to prove or disprove by magnetoreflection[6,12] measurements.

I wish to thank W. Goldburg for reading the manuscript.

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Pseudopotential Calculation of the Thermal Expansion Coefficient of Sodium and Potassium*

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The total adiabatic potential is represented by a model based on electrostatic interactions among the ions and conduction electrons, Born-Mayer repulsion between the ions, a local pseudopotential interaction between ion cores and conduction electrons, and conduction-electron kinetic, exchange, and correlation energies. The three model parameters are determined for sodium and potassium by requiring agreement with the crystal binding energy and its first two volume derivatives at zero temperature and pressure. The phonon frequencies and Grüneisen parameters, the bulk-modulus pressure derivative, and the thermal expansion coefficient as a function of temperature are then calculated. These calculations are in good qualitative agreement with experimental results.

I. INTRODUCTION

The aim of our present research program is to begin with the atomic description of crystals and calculate the thermodynamic properties. For nearly-free-electron metals it is convenient to describe the mechanical system of ions, electrons, and forces by means of pseudopotential perturbation theory. Thermodynamic functions may then be calculated by lattice dynamics theory.

Simple local pseudopotential models have been used to calculate the phonon spectrum of several metals,[1–7] and reasonably good agreement with experiment has been obtained. In the present paper we calculate the spectrum of Grüneisen parameters for sodium and potassium; this calculation may be compared with experiment in the form of the thermal expansion coefficient as a function of temperature. We have chosen to use Harrison's[1] modified point-ion pseudopotential, with two adjustable parameters, and we also include a Born-Mayer repulsion between ion cores, with one adjustable parameter.

Since we want our theory to be consistent with all the thermodynamic properties, the adjustable parameters are determined to obtain agreement with the measured crystal binding energy, lattice spacing, and compressibility at zero temperature and pressure. With

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the parameters so determined, comparison between calculated and measured anharmonic properties is a meaningful test of the theory.

II. LOCAL PSEUDOPOTENTIAL FORMULATION OF THE ENERGY

We consider a metal containing N similar atoms, each atom contributing Z conduction electrons. The basic approximations in the description of this system are the rigid ion approximation, the adiabatic approximation, and the one-electron approximation. The conduction-electron energies are then derived by perturbation theory to second order in the pseudopotential.[1,8] We then assume the pseudopotential is a real, local potential. Note this assumption implies the pseudo-wave functions are equal to the true conduction-electron wave functions. The total adiabatic potential for the ions is U, and is composed of the ion-ion potential U_I plus the total conduction-electron energy U_E:

$$U=U_I+U_E. \tag{2.1}$$

We will list the detailed contributions to these potentials.

The ion-ion potential includes the overlap repulsion U_R, for which we take the Born-Mayer model,[9] and the electrostatic energy U_{ES}, as calculated by Fuchs[10] for point ions of charge $+Ze$ in a uniform negative compensating charge.

$$U_I=U_R+U_{ES}. \tag{2.2}$$

The ions, labeled by the index n, are located at the arbitrary positions $\mathbf{r}_n$. Then the repulsive energy is

$$U_R=\tfrac{1}{2}\sum\nolimits'_{nn'}\alpha\exp(-\gamma|\mathbf{r}_n-\mathbf{r}_{n'}|), \tag{2.3}$$

where $\sum'_{nn'}$ excludes $n=n'$, and α, γ are positive parameters. The electrostatic energy may be written

$$\begin{aligned}U_{ES}=N(Z^2e^2/2)\{(4\pi/\Omega_a)\textstyle\sum'_{\mathbf{q}}S_{\mathbf{q}}S_{-\mathbf{q}}q^{-2}\exp(-q^2/4\eta^2)\\+N^{-1}\textstyle\sum'_{nn'}|\mathbf{r}_n-\mathbf{r}_{n'}|^{-1}\operatorname{erfc}(\eta|\mathbf{r}_n-\mathbf{r}_{n'}|)\\-[(2\eta/\sqrt{\pi})+(\pi/\eta^2\Omega_a)]\},\end{aligned} \tag{2.4}$$

where

$$S_{\mathbf{q}}=N^{-1}\sum\nolimits_n\exp(-i\mathbf{q}\cdot\mathbf{r}_n). \tag{2.5}$$

Here Ω_a is the volume per atom and η is the Ewald convergence factor; note U_{ES} is independent of η. The $\sum'_{\mathbf{q}}$ is over all wave vectors $\mathbf{q}$ except $\mathbf{q}=0$. If the configuration of ions forms a perfect lattice, then the structure factor $S_{\mathbf{q}}$ equals $\delta_{\mathbf{q},\mathbf{Q}}$, where $\mathbf{Q}$ is any reciprocal lattice vector.

The total conduction-electron energy is conveniently expressed in terms of the matrix elements w_{Bq} of the bare single-ion pseudopotential. We write the total electron energy, evaluated in the electronic ground state, as a uniform-electron-gas part U_{EG} and a band-structure part U_{BS}.

$$U_E=U_{EG}+U_{BS}. \tag{2.6}$$

The electron-gas energy is

$$U_{EG}=NZ[(3/5)\epsilon_F+\epsilon_X+\epsilon_C+w_{C0}]. \tag{2.7}$$

Here the kinetic energy per electron is $\frac{3}{5}\epsilon_F=\frac{3}{5}(\hbar^2k_F^2/2m)$, where k_F is the Fermi wave-vector magnitude and m is the electron mass. The uniform-electron-gas exchange and correlation energies per electron are ϵ_X and ϵ_C, respectively. The final term w_{C0} in (2.7) is the $\mathbf{q}=0$ matrix element of the ion-core part (non-Coulomb part) of w_B.

The band-structure energy is[1]

$$U_{BS}=N\sum\nolimits'_{\mathbf{q}}S_{\mathbf{q}}S_{-\mathbf{q}}F_q, \tag{2.8}$$

where F_q is the energy–wave-number characteristic

$$F_q=-\frac{\Omega_aq^2}{8\pi e^2}\frac{w_{Bq}w_{B-q}(f_q-1)}{[1+(f_q-1)(1-g_q)]}, \tag{2.9}$$

$$f_q-1=\frac{2me^2k_F}{\pi\hbar^2q^2}\left[\frac{4k_F^2-q^2}{4k_Fq}\ln\left|\frac{2k_F+q}{2k_F-q}\right|+1\right]. \tag{2.10}$$

Here f_q is the Hartree dielectric function. The factor $(1-g_q)$ in F_q represents an approximate correction to the exchange and correlation energy of the conduction-electron gas, due to the nonuniformity of the gas (note this factor appears in U_{BS} for $q\neq0$). Following Hubbard[11] and Sham,[2] a reasonable form for g_q is

$$g_q=q^2/2(q^2+\xi k_F^2). \tag{2.11}$$

We have determined the parameter ξ in the following way: According to lattice dynamics theory[12] the compressibility should be the same when calculated directly from the second volume derivative of the total potential U, or when calculated from the method of long waves. The exchange and correlation contribution arises in the first calculation from the term $(\epsilon_X+\epsilon_C)$ in (2.7), and in the second calculation from the function g_q in (2.9), through (2.8). The requirement that these agree fixes ξ. The result for ξ depends on the form used for ϵ_C, and is given in Sec. III below. We note the result is identical (for any ϵ_C) to the ξ determined by Geldart and Vosko[13] from the electron-gas compressibility.

We have chosen Harrison's[1] modified point-ion model for the present calculations; accordingly the pseudopotential matrix elements are given by

$$w_{Bq}=\frac{1}{\Omega_a}\left[-\frac{4\pi Ze^2}{q^2}+\frac{\beta}{(1+q^2\rho^2)^2}\right]. \tag{2.12}$$

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Here β and ρ are parameters which we determine below by fitting the observed crystal energy and its volume derivatives. For $q=0$, the ion-core part which appears in (2.7) is just

$$w_{C0}=\beta/\Omega_a. \qquad (2.13)$$

III. CALCULATION OF THE ENERGY AND ITS VOLUME DERIVATIVES

We first simplify the total adiabatic potential per ion, U/N, for a bcc lattice. It is convenient to introduce r_s, the radius of the sphere whose volume is the average conduction-electron volume:

$$(4\pi r_s^3/3)=\Omega_a/Z. \qquad (3.1)$$

With r_s in units of the Bohr radius (a_0) and with energies in Rydbergs ($e^2/2a_0$), the contributions to the total potential are as follows:

$$N^{-1}U_R=\tfrac{1}{2}\sum{}'_n\,\alpha\exp(-\gamma|r_n|), \qquad (3.2)$$

$$N^{-1}U_{ES}=1.79186(Z^{5/3}/r_s)\quad\text{(Ref. 10)}, \qquad (3.3)$$

$$N^{-1}U_{EG}=Z[(2.21/r_s^2)-(0.916/r_s) -(0.115\text{–}0.031\ln r_s)+(\beta/\Omega_a)], \qquad (3.4)$$

$$N^{-1}U_{BS}=\sum{}'_Q F_Q. \qquad (3.5)$$

In evaluating the Born-Mayer repulsive energy (3.2) we have taken $\sum'_n$ over nearest and next-nearest neighbors. In addition, from studies of the ionic potentials for alkali halides as reviewed by Tosi,[14] we take a fixed value of γ for both sodium and potassium:

$$1/\gamma=0.339\times10^{-8}\text{ cm}. \qquad (3.6)$$

In (3.4), the first term in square brackets is $\frac{3}{5}\epsilon_F$, the second is ϵ_X, and the third is the Pines-Nozières[15] interpolation approximation for ϵ_C. With this form for ϵ_C, the parameter ξ of (2.11) is given by

$$\xi=0.916/(0.458+0.012r_s). \qquad (3.7)$$

Finally in (3.5) the $\sum'_Q$ is over all reciprocal lattice vectors except $Q=0$.

The total adiabatic potential may be compared with measured quantities at zero temperature and pressure by means of the following equations:

$$(U/N)=-BE-I_Z, \qquad (3.8)$$

$$\Omega_a[d(U/N)/d\Omega_a]=-\Omega_a P=0, \qquad (3.9)$$

$$\Omega_a^2[d^2(U/N)/d\Omega_a^2]=\Omega_a B_0. \qquad (3.10)$$

In (3.8) the binding energy per atom of metal is BE, a positive quantity, and the ionization energy for each ion is I_Z. We have neglected the zero-point vibrational energy in (3.8), since this is about 0.001 Ry for Na and K. Equation (3.9) is the requirement that the pressure P is zero, and (3.10) gives the bulk modulus at zero temperature and pressure, B_0. Zero-point vibrational contributions have also been neglected in (3.9) and (3.10).

TABLE I. Experimental data used in the present analysis. All quantities are estimated at $T=0$°K, except for $\langle\omega^2\rangle$, which is based on neutron scattering measurements at 90°K for Na and 9°K for K.

Quantity	Na	K
Z	1	1
$\Omega_a(a_0^3)$	255.5[a]	485.3[b]
$r_s(a_0)$	3.937	4.875
ξ	1.81	1.77
BE (Ry)	0.08[c]	0.07[c]
I_Z (Ry)	0.38[d]	0.32[d]
B_0 (10^{10} dyne/cm^2)	7.41[a,e]	3.67[b,f]
$\langle\omega^2\rangle$ (10^{26} sec^{-2})	2.87[g]	1.07[h]

[a] Reference 20.
[b] Reference 22.
[c] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Natl. Bur. Std. (U.S.), Circ. **500** (1952).
[d] C. E. Moore, Natl. Bur. Std. (U.S.), Circ. **467** (1949).
[e] Reference 21.
[f] Reference 23.
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[h] R. A. Cowley, A. D. Woods, and G. Dolling, Phys. Rev. **150**, 487 (1966).

We have determined the three parameters α, β, ρ by fitting the experimental quantities on the right-hand sides of (3.8)–(3.10). The experimental data are listed in Table I. In this fitting procedure we found that agreement between theory and experiment could be obtained for small variations of the parameters. For potassium, for example, the calculated quantities remain unchanged for correlated variations of α, β, ρ within the limits ±25, ±4, ±0.04, respectively (see Table II for units). We also found that this small arbitrariness of the parameters was removed by requiring agreement between calculated and measured values of the average of the phonon frequencies squared, denoted by $\langle\omega^2\rangle$. Experimental values of $\langle\omega^2\rangle$, determined by inelastic neutron scattering measurements, are given in Table I. The calculation of $\langle\omega^2\rangle$ is outlined in Sec. IV below. The parameters α, β, ρ determined in this way are listed in Table II.

The various calculated contributions to the total potential and its volume derivatives are listed in Table III. Several interesting results for Na and K may be observed from this table. First, although the various contributions to the uniform-electron-gas energy U_{EG} are not small, they nearly cancel, and the total binding

TABLE II. The Born-Mayer repulsion coefficient α and the modified point-ion pseudopotential parameters β and ρ, determined to obtain agreement with measured values of (U/N), $P=0$, B_0, and $\langle\omega^2\rangle$.

Parameter	Na	K
α (Ry)	10.5	124
β (Ry a_0^3)	37	66
ρ (a_0)	0.50	0.69

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[14] M. P. Tosi, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 1.

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TABLE III. Calculated contributions to the energy and its volume derivatives at $T=0°\text{K}$. All quantities are in Ry.

Energy contribution	Na			K		
	(U/N)	$\Omega_a P$	$\Omega_a B_0$	(U/N)	$\Omega_a P$	$\Omega_a B_0$
$\frac{3}{5}\epsilon_F$	0.14_5	−0.095	0.159	0.09	−0.062	0.103
ϵ_X	−0.23	0.078	−0.103	−0.19	0.063	−0.084
ϵ_C	−0.07	0.010	−0.010	-0.06_5	0.010	−0.010
β/Ω_a	0.15	−0.145	0.290	0.14	−0.136	0.272
$N^{-1}U_{EG}$	-0.00_5	−0.152	0.336	-0.02_5	−0.125	0.281
$N^{-1}U_{BS}$	−0.00	0.004	−0.021	−0.00	0.005	−0.017
$N^{-1}U_R$	+0.00	−0.004	0.016	+0.00	−0.004	0.020
$N^{-1}U_{ES}$	-0.45_5	0.152	−0.202	-0.36_5	0.123	−0.163
Total	−0.46	0.000	0.129	−0.39	−0.001	0.121
Experiment	−0.46	0.000	0.129	−0.39	0.000	0.121

energy of the crystal is due almost entirely to the electrostatic energy U_{ES} of the lattice of point ions imbedded in a uniform negative background charge. On the other hand, the contributions of the uniform-electron-gas energy and of the electrostatic energy to the pressure (first volume derivative of the total potential) are nearly equal and opposite. The smallness of the band-structure energy contribution to all of the energy derivatives is in agreement with the nearly-free-electron characteristics of the alkali metals. Finally we note the band structure and Born-Mayer repulsive energies are of increasing relative importance in higher volume derivatives of the energy; this indicates their importance in the anharmonic properties.

The screened pseudopotential form factors for Na and K, calculated with β, ρ listed in Table II, are in qualitative agreement for $0\leq q\leq 2k_F$ with the Heine-Abarenkov form factors listed by Harrison.[1]

IV. CALCULATED PHONON FREQUENCIES AND ANHARMONIC PROPERTIES

In Sec. II, the total adiabatic potential was given for arbitrary positions of the ions. From this expression we may calculate the harmonic potential energy coefficients, evaluate them in the perfect lattice configuration, and construct the dynamical matrices $\mathbf{a}_\mathbf{k}$ for all phonon wave vectors $\mathbf{k}$ in the first Brillouin zone. The $\mathbf{a}_\mathbf{k}$ are real symmetric 3×3 matrices whose eigenvectors are the phonon polarization vectors $\mathbf{v}_{\mathbf{k}s}$, $s=1$, 2, 3, and whose eigenvalues are $M\omega_{\mathbf{k}s}^2$, with $M=$ mass of the ions and $\omega_{\mathbf{k}s}=$ phonon circular frequencies. Since we assume periodic boundary conditions in arriving at the phonon solutions, the potential energy coefficients are calculated at fixed volume and there is no contribution from the uniform-electron-gas energy. Detailed contributions to $a_{\mathbf{k},ii'}$, where i, i' are Cartesian indices specifying the matrix elements, are found to be as follows:

Born-Mayer repulsion contribution.

$$\alpha\gamma \textstyle\sum'_n \cos(\mathbf{k}\cdot\mathbf{r}_n)\exp(-\gamma r_n)\{(1/r_n)\delta_{ii'} -[\gamma+(1/r_n)](r_{ni}r_{ni'}/r_n^2)\} +\tfrac{1}{3}\alpha\gamma\textstyle\sum'_n \exp(-\gamma r_n)[\gamma-(2/r_n)]\delta_{ii'}. \quad (4.1)$$

Electrostatic energy contribution.

$$Z^2e^2\textstyle\sum'_n\cos(\mathbf{k}\cdot\mathbf{r}_n)\{[(2\eta/(\sqrt{\pi})r_n^2)\exp(-\eta^2r_n^2) +(1/r_n^3)\operatorname{erfc}(\eta r_n)]\delta_{ii'}-[[(4\eta^3/(\sqrt{\pi})) +(6\eta/(\sqrt{\pi})r_n^2)]\exp(-\eta^2r_n^2)+(3/r_n^3)\operatorname{erfc}(\eta r_n)] \times(r_{ni}r_{ni'}/r_n^2)\}+(4\pi Z^2e^2/\Omega_a)\textstyle\sum_\mathbf{Q}\exp[-(\mathbf{Q}+\mathbf{k})^2/4\eta^2] \times[(\mathbf{Q}+\mathbf{k})_i(\mathbf{Q}+\mathbf{k})_{i'}/(\mathbf{Q}+\mathbf{k})^2]+(4Z^2e^2/3) \times[(\pi/\Omega_a)-(\eta^3/\sqrt{\pi})]\delta_{ii'}. \quad (4.2)$$

Band-structure energy contribution.

$$2\textstyle\sum_\mathbf{Q} F_{Q+k}(\mathbf{Q}+\mathbf{k})_i(\mathbf{Q}+\mathbf{k})_{i'}-\tfrac{2}{3}\textstyle\sum'_\mathbf{Q} F_Q Q^2\delta_{ii'}. \quad (4.3)$$

Here we have used $r_n=|\mathbf{r}_n|$. Although our derivation is in principle different from Sham's,[2] the above results agree with his local pseudopotential results, except for the difference in our parameter ξ.

The average phonon frequency squared is simply obtained from the average over $\mathbf{k}$ of the trace of the dynamical matrices, and is given by

$$3M\langle\omega^2\rangle=\alpha\gamma\textstyle\sum'_n\exp(-\gamma r_n)[\gamma-(2/r_n)] +2\textstyle\sum_\mathbf{q} q^2F_q(N^{-1}-\delta_{\mathbf{q},\mathbf{Q}}). \quad (4.4)$$

The individual phonon Grüneisen parameters are $\gamma_{\mathbf{k}s}$, defined by

$$\gamma_{\mathbf{k}s}=-(d\ln\omega_{\mathbf{k}s}/d\ln\Omega_a). \quad (4.5)$$

These quantities may be calculated from the Hellmann-Feynman theorem,[16,17] as we have done previously.[18] In matrix notation, with indices suppressed, the diagonalization of a dynamical matrix is represented by

$$\mathbf{v}^{-1}\mathbf{a}\mathbf{v}=M\omega^2, \quad (4.6)$$

where the right-hand side is a diagonal matrix. The volume derivatives of the eigenvalues are then given by diagonal elements of the matrix equation

$$\mathbf{v}^{-1}[d\mathbf{a}/d\Omega_a]\mathbf{v}=M[d\omega^2/d\Omega_a]. \quad (4.7)$$

The individual $\gamma_{\mathbf{k}s}$ were calculated in this way.

With the parameters as determined in Sec. III, we have calculated the phonon frequencies to an accuracy of 0.5% and the Grüneisen parameters to an accuracy of 1%, for sodium and potassium at 505 $\mathbf{k}$ vectors in (1/48) of the first zone. The frequencies are compared to inelastic neutron scattering measurements in Figs. 1 and 2. The over-all agreement is fair, but not within experimental error. By slight adjustments of the parameters α, β, and ρ, we can bring the calculated curves into agreement with the measurements within experimental error, except that our simple model does not show the observed kink in the longitudinal [001] branch. The calculated Grüneisen parameters along symmetry axes are shown in Figs. 3 and 4. These quantities are all positive and show large variations over

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[16] H. Hellmann, *Einfuhrung in die Quantenchemie* (Franz Deuticke, Leipzig, 1937).

[17] R. P. Feynman, Phys. Rev. **56**, 340 (1939).

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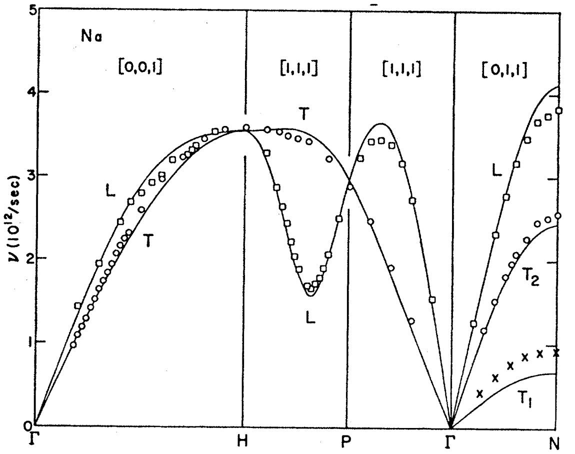

FIG. 1. Calculated phonon dispersion curves (solid lines) compared with the 90°K measurements of Woods *et al.* [Phys. Rev. **128**, 1112 (1962)] for Na.

the zone. All the calculated $\gamma_{\mathbf{k}s}$ lie in the range $\sim$0.9 to $\sim$1.8 for Na and $\sim$0.95 to $\sim$1.7 for K. The average $\gamma_{\mathbf{k}s}$, averaged over the first zone, is 1.18 for sodium and 1.21 for potassium.

We have calculated two anharmonic quantities which may be compared with measured results. The first is the pressure derivative of the bulk modulus; for zero temperature and pressure this may be written

$$(dB/dP)+1=-[\Omega_a^3d^3(U/N)/d\Omega_a^3]/[\Omega_a^2d^2(U/N)/d\Omega_a^2]. \tag{4.8}$$

At finite temperatures, (4.8) is the main contribution to the pressure derivative of either the isothermal (B_T) or the adiabatic (B_S) bulk modulus. Our calculations of (4.8) are compared with measured room-temperature results in Table IV; the agreement is quite satisfactory.

The thermal expansion coefficient β is most conveniently calculated from the thermodynamic equation

$$\beta B_T=-(\partial^2F/\partial T\partial\Omega)_{\Omega,T}, \tag{4.9}$$

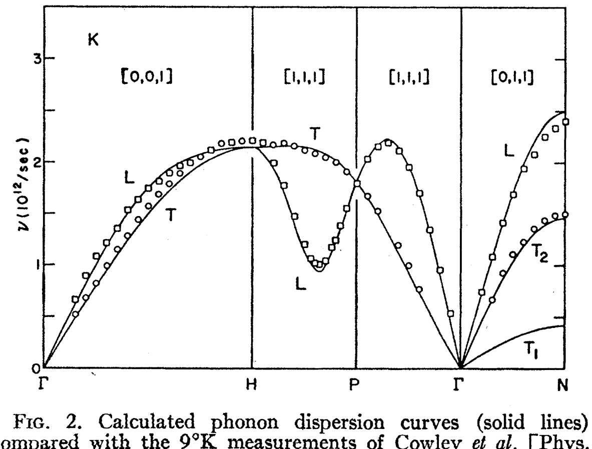

FIG. 2. Calculated phonon dispersion curves (solid lines) compared with the 9°K measurements of Cowley *et al.* [Phys. Rev. **150**, 487 (1966)] for K.

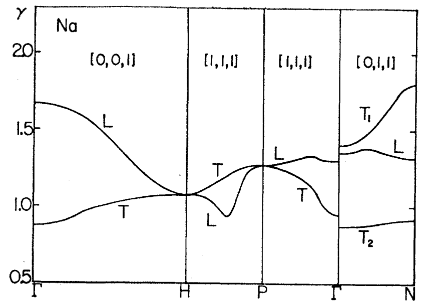

FIG. 3. Calculated Grüneisen parameters for Na.

where B_T is the isothermal bulk modulus, F is the total Helmholtz free energy, T is the temperature, and Ω is the total volume. We neglect the explicit anharmonic contribution, which arises from the anharmonic free energy,[18] and the electronic excitation contribution, since these are quite small for Na and K up to room temperature. The resulting quasiharmonic lattice-dynamical contribution is expressed in the dimensionless quantity

$$(\beta B_T\Omega_a/3k)=(3N)^{-1}\textstyle\sum_{\mathbf{k},s}\gamma_{\mathbf{k}s}(\hbar\omega_{\mathbf{k}s}/kT)^2\bar{n}_{\mathbf{k}s}(\bar{n}_{\mathbf{k}s}+1), \tag{4.10}$$

where k is Boltzmann's constant and

$$\bar{n}_{\mathbf{k}s}=[\exp(\hbar\omega_{\mathbf{k}s}/kT)-1]^{-1}. \tag{4.11}$$

We note in the high-temperature limit (4.10) becomes the macroscopic Grüneisen constant.

We have calculated (4.10) for bcc Na and K at fixed volume, namely, the zero temperature and pressure volume listed in Table I. These calculations are compared with the corresponding measured quantity in Figs. 5 and 6. The experimental data used was β for Na from Siegel and Quimby[19] (75–300°K), B_T for Na from Refs. 20 and 21; β for K was calculated from the volume-versus-temperature data of Ref. 22, B_T for K

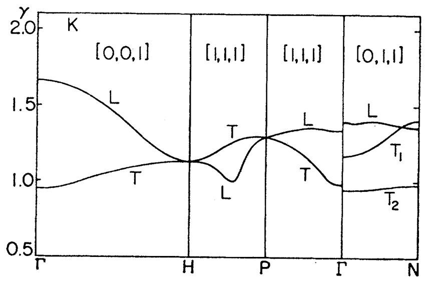

FIG. 4. Calculated Grüneisen parameters for K.

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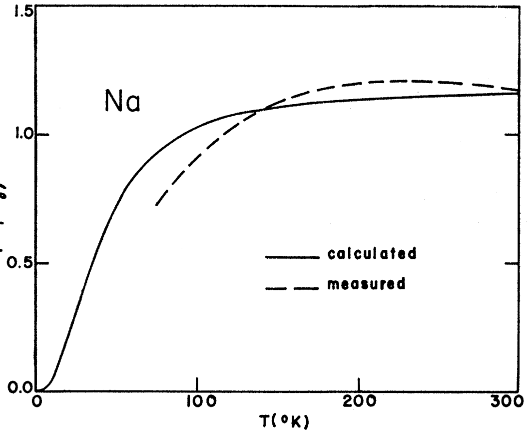

FIG. 5. Calculated (solid line) and measured (dashed line) curves of the thermal expansion coefficient, in the form of $(\beta B_T\Omega_a/3k)$ at fixed volume, for Na.

from Refs. 22 and 23. The experimental curve was corrected thermodynamically to the fixed volume in a manner described previously.[24]

The agreement between theory and experiment is within experimental error in the high-temperature region for both Na and K. At intermediate temperatures, however, the calculated curves are too high. Furthermore, the over-all agreement cannot be improved substantially by varying the parameters α, β, and ρ. Our interpretation of this discrepancy is that we do not have the correct dispersion of the $\gamma_{\mathbf{k}s}$ in the intermediate-to-small **k** region.

V. SUMMARY AND COMMENTS

We have studied the energy and lattice dynamics of bcc Na and K, for a simple model based on electrostatic and Born-Mayer repulsive energies between the ions and a modified point-ion pseudopotential. The model parameters were fixed to obtain agreement with the measured crystal binding energy and its first two volume derivatives. We then calculated the spectrum of phonon frequencies and Grüneisen parameters, the pressure derivative of the bulk modulus, and the thermal expansion coefficient for temperatures up to room temperature. Two discrepancies between measurements and our calculations are apparent.

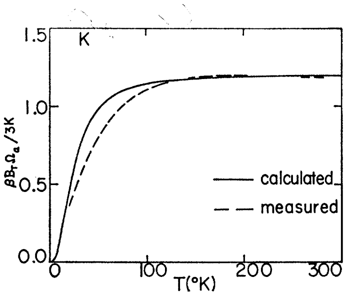

FIG. 6. Calculated (solid line) and measured (dashed line) curves of thermal expansion coefficient, in the form of $(\beta B_T\Omega_a/3k)$ at fixed volume, for K.

TABLE IV. Comparison of calculated and measured pressure derivatives of the bulk modulus.

Quantity	Sodium	Potassium
$(\partial B_T/\partial P)_T$(300°K)	3.95[a]	3.85[b]
$(\partial B_S/\partial P)_T$ (300°K)	3.60[c]	3.97[d]
(dB/dP) (Calculated, 0°K)	3.63	3.83

[a] Reference 20.
[b] Reference 22.
[c] W. B. Daniels, Phys. Rev. **119**, 1246 (1960).
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First, the calculated thermal expansion coefficient is somewhat high at intermediate temperatures for both Na and K; this indicates that some of the calculated Grüneisen parameters are too high. The second discrepancy concerns the heat capacity and elastic constants. We have extracted the lattice specific heat at constant volume from the measurements of Martin[25]; the corresponding Debye temperatures are in good agreement with our calculations except at low temperatures (<10°K for Na; <6°K for K). Along with this we have found the calculated elastic constants to differ from the low-temperature experimental results by $\approx 5\%$. Such discrepancies reflect the limitations of the local pseudopotential and the approximate treatment of the conduction-electron exchange and correlation.

In comparing theory and experiment for the thermal expansion coefficient, the function $(\beta B_T\Omega_a/3k)$ was studied because it is theoretically simple; according to (4.10) it is just a weighted average of the phonon Grüneisen parameters. In addition, the zero-pressure experimental data were corrected thermodynamically to fixed volume conditions without increasing the experimental uncertainty of the curve. This was possible because of the smallness of this volume correction.[24]

Finally, we note the Born-Mayer repulsive exponent γ was taken as fixed in the calculations described here. Allowing γ to vary has no essential effect on the general results; if we decrease γ and repeat the calculations, we find that α decreases accordingly, β and ρ remain nearly the same, and the calculated results are essentially unchanged.

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