*Supported by the National Science Foundation under Grant No. GP 13632.

[1] C. Y. Fong and M. L. Cohen, Phys. Rev. Letters 24, 306 (1970).

[2] M. L. Cohen and V. Heine, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 37.

[3] C. Y. Fong, M. L. Cohen, R. R. L. Zucca, J. Stokes, and Y. R. Shen, Phys. Rev. Letters 25, 1486 (1970); J. Stokes, Y. R. Shen, Y. W. Tsang, M. L. Cohen, and C. Y. Fong, Phys. Letters 38A, 347 (1972).

[4] C. Y. Fong and M. L. Cohen, Phys. Letters (to be published).

[5] For example, U. Gerhardt, Phys. Rev. 172, 651 (1968).

[6] For example, N. V. Smith, Phys. Rev. B 3, 1862 (1971).

[7] T. H. Geballe, B. T. Matthias, J. P. Remeika, A. M. Clogston, V. B. Compton, J. P. Maita, and H. J. Williams, Physics 2, 293 (1966).

[8] L. F. Mattheiss, Phys. Rev. B 5, 315 (1972).

[9] K. Schwarz, Monatsh. Chem. 102, 1400 (1972).

[10] L. A. Hemstreet, Jr. and C. Y. Fong, Phys. Rev. B 6, 1464 (1972).

[11] L. Pauling, The Nature of the Chemical Bond, 3rd ed. (Cornell U. P. , Ithaca, N. Y., 1960), p. 514.

[12] D. Brust, Phys. Rev. 134, A1337 (1964).

Calculation of the Cohesive Energies and Bulk Properties of the Alkali Metals*

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The cohesive energy and zero-pressure density of the alkali metals have been calculated using the self-consistent augmented-plane-wave method and the statistical $(X\alpha)$ exchange-correlation approximation. For the value of α which makes a single determinant of atomic spin orbitals satisfy the virial theorem, the lighter alkali metals are computed to have cohesive energies and zero-pressure densities which are too large (errors of 22 and 16% for Li) with respect to experiment. To test the sensitivity of these results to the choice of α, the same calculations have been performed with α set equal to $\frac{2}{3}$. This choice of α produced more uniformly good results for all the alkali metals with the largest errors occurring for cesium (errors of 7 and 9%, respectively). It is suggested that these results may be a consequence of the large change in the valence electronic charge density that occurs when the lighter alkali-metal atoms come together to form the solid. It is not suggested, however, that $\alpha = \frac{2}{3}$ be used in all energy-band calculations.

I. INTRODUCTION

In recent years an approximate method[1] (called the $X\alpha$ method) has been developed for calculating the bulk properties of solids under pressure. The method is essentially one in which the exchange-correlation potential energy in a one-electron effective Schrödinger equation is approximated by a term proportional to the one-third power of the total electron charge density. The $X\alpha$ approximation has already been applied to several solids with varying degrees of success,[2-5] but there is still a great deal of uncertainty both as to the accuracy and to the range of applicability of the method. It appeared that it would be informative to apply the $X\alpha$ method to a whole family of closely related solids. Specifically, it was hoped that some understanding could be gained from the way the $X\alpha$ method treated the various members of the family, and that perhaps some general over-all trends might be made manifest.

The obvious choice for such a family of solids is the alkali metals. Because of their relative simplicity, the alkali metals have long been a testing ground for new approximate methods in solid-state theory. Furthermore, there is now an abundance of experimental information[6,7] available on these metals.

II. DESCRIPTION OF THE CALCULATION

In the $X\alpha$ approximation, the total energy of a crystal may be written[2,3,8,9]

$$\langle E_{X\alpha}\rangle = \langle T_{X\alpha}\rangle + \langle U_{X\alpha}\rangle , \tag{1}$$

where $\langle T_{X\alpha}\rangle$ is the total kinetic energy and $\langle U_{X\alpha}\rangle$ is the total potential energy of the crystalline system.

The total electronic charge density at the point 1 is assumed to be related to a set of one-electron wave functions by the expression

$$\rho(1) = \sum_i n_i u_i^*(1) u_i(1) . \tag{2}$$

In this expression, n_i is the occupation number of the ith one-electron state. If we assume the nuclei to be fixed, then $\langle T_{X\alpha} \rangle$ is just the total kinetic energy of the electrons. In Ry energy units,

$$\langle T_{X\alpha} \rangle = - \sum_i n_i \int u_i^*(1) \nabla_1^2 u_i(1) dv_1 . \tag{3}$$

The potential energy $\langle U_{X\alpha} \rangle$ can be conveniently expressed as a sum of four terms:

$$\langle U_{X\alpha} \rangle = U_{en} + U_{nn} + U_{ee} + U_{xc} , \tag{4}$$

where U_{en} is the interaction energy of the charge density $\rho(1)$ with the nuclei, V_{nn} is the potential energy of interaction of the nuclei with one another, and U_{ee} is the classical electrostatic energy of interaction of the charge density $\rho(1)$ with itself. Finally, U_{xc} is the $X\alpha$ approximation to the exchange-correlation energy (and self-energy correction) of the electrons. We will assume that spin polarization of the charge density is unimportant, in which case

$$U_{xc} = - \frac{1}{2} \int \rho(1) \left[9\alpha \left(\frac{3}{8\pi} \rho(1) \right)^{1/3} \right] dv_1 . \tag{5}$$

An effective Schrödinger equation for the set of occupied one-electron wave functions in Eq. (2) is obtained by varying $\langle E_{X\alpha} \rangle$ in the usual manner while constraining the occupation numbers to remain unchanged. The resulting one-electron equation must in general be solved in an iterative fashion.

Slater[10] has shown that an equilibrium state of an electronic system in the $X\alpha$ scheme is obtained when the occupation numbers in Eq. (2) obey Fermi statistics. In the work reported here, we were interested in the zero-temperature properties of the alkali metals. Therefore, at each stage of iteration the set of n_i's was chosen according to zero-temperature Fermi statistics.[11]

From thermodynamics, the pressure acting on a system in equilibrium at zero temperature is defined to be equal to the negative of the volume derivative of the total energy of the system. In the $X\alpha$ approximation, this relation is

$$P = - \frac{d\langle E_{X\alpha} \rangle}{dV} . \tag{6}$$

Fortunately, the pressure in the $X\alpha$ approximation can be expressed in a form which is in some ways more computationally convenient. It can be shown[2,9,12] that the self-consistent solution of the one-electron Schrödinger equation satisfies a virial theorem of the form

$$PV = \frac{1}{3} (2\langle T_{X\alpha} \rangle + \langle U_{X\alpha} \rangle) . \tag{7}$$

Both expressions for the pressure have their relative merits. Equation (7) has the advantage that it requires explicit knowledge of the system at only the volume V, whereas Eq. (6) requires knowledge of $\langle E_{X\alpha} \rangle$ as a function of the volume in the neighborhood of V. On the other hand, Eq. (7) for the pressure is susceptible to the computational errors in $\langle T_{X\alpha} \rangle$ and $\langle U_{X\alpha} \rangle$. According to the variational principle, these errors will tend to be larger than those in $\langle E_{X\alpha} \rangle$.[13]

The cohesion of an elemental crystal is defined theoretically to be the difference between the total energy per atom of the crystal and the total energy of the isolated atom in its ground state. In the $X\alpha$ method, the cohesion can be expressed as

$$C = \langle E_{X\alpha} \rangle_a - \langle E_{X\alpha} \rangle_c , \tag{8}$$

where we will adopt the approximation of using the same value for α in both atomic and crystalline calculations. In this paper, the cohesive energy is defined to be the maximum value of the cohesion.

In the work reported here, the lattice structure was chosen to be the experimentally observed bcc arrangement of the alkali metals. At each lattice constant, a starting potential for initiating the iterative solution of the one-electron equation was generated by superimposing self-consistent atomic charge densities obtained from a Herman–Skillman[14] calculation. The one-electron equation was then solved by an iterative procedure using the augmented-plane-wave (APW) expansion method of Slater.[15] The APW basis set was chosen to be large enough to assure that the kinetic energy would be converged to less than 0.001 Ry. For the sake of simplifying the computations, the muffin-tin approximation[16] was made, with the radius of the muffin-tin sphere in all cases chosen to be equal to one-half of the nearest-neighbor distance.

Two approaches to the selection of α were taken in this work. One of the methods was to choose α to be the value α_{vt}, which makes the total $X\alpha$ energy of the isolated alkali metal atom equal to the total energy of a determinantal wave function with the occupied $X\alpha$ wave functions as the space part of the spin orbitals.[17] Schwarz[18] has determined α_{vt} for the alkali metals lithium, sodium, potassium, and rubidium. He found that for a given atom, α_{vt} was very close to the value of α which made the total $X\alpha$ energy equal to the total Hartree–Fock energy calculated by Mann.[19] The value of α_{vt} for cesium was reported in a previous paper by the present author to be 0.69941.[5] The other option that was studied is to choose α to have the value $\frac{2}{3}$ as suggested by Kohn and Sham[20] and Gaspar.[21]

In the lighter alkali metals, the largest single source of computational error is believed to be in the finite sampling of the Brillouin zone associated

with the valence band. Calculations of states within this band were performed at the equivalent of 128 uniformly spaced points in the full zone. For all the alkali metals, it was found that the first s band and the first p band under the valence band were narrow enough to be adequately sampled by 16 uniformly spaced points in the Brillouin zone. All other core states were treated in an atomiclike manner but in the crystalline self-consistent potential.

The computations were carried out on an IBM 360/65 computer using double-precision arithmetic. The numerical operations in both the atomic and crystalline problems were performed on the Herman–Skillman radial mesh.[14] In the heavier alkali metals, the errors introduced by this finite radial mesh were about as large as those introduced by the Brillouin-zone sampling. Within the model system employed, the numerical errors in the computed cohesions and pressures of lithium are believed to be no more than 0.003 Ry and 1.5 kbar, respectively. Similarly, for cesium the errors should be no greater than 0.002 Ry and 1.0 kbar. The errors in the computed cohesions and pressures of the other alkali metals should lie between those of lithium and cesium.

III. RESULTS

For each of the alkali metals, two calculations of the theoretical cohesion and pressure were performed at the experimentally observed[6] low-temperature zero-pressure lattice constant. In one set of calculations, α was chosen to be equal to α_{vt} (Table I, top-half) and, in the other, α was chosen to be equal to $\frac{2}{3}$ (Table I, bottom-half). Further calculations were performed on the lithium and cesium systems at other lattice constants so that the volume dependence of the total energy and

TABLE I. Theoretical results at the experimentally observed zero-pressure densities. Here a negative % error for a quantity implies that its magnitude in the $X\alpha$ approximation was smaller than the experimental value.

Alkali metal		$X\alpha$ cohesion (Ry)	% error cohesion	$X\alpha$ pressure (kbar)	% error density[a]
Li	$\alpha = \alpha_{vt}$	0.148	+22	−20.7	+16
Na		0.096	+16	−6.3	+7
K		0.075	+9	−1.4	+3
Rb		0.066	+3	+0.1	−1
Cs		0.061	+1	−0.1	+2
Li	$\alpha = \frac{2}{3}$	0.124	+2	+2.2	−2
Na		0.087	+5	+0.5	−1
K		0.068	−1	+1.6	−3
Rb		0.061	−5	+2.0	−6
Cs		0.057	−7	+1.2	−9

[a]Errors given for Na, K, and Rb are estimates.

TABLE II. Information on the alkali metals.

Alkali metal	Atomic No.	α_{vt} [a]	Experimental lattice[b] constant (a.u.)	Experimental cohesive[c] energy (Ry)
Li	3	0.780 87	6.597	0.121
Na	11	0.730 44	7.984	0.083
K	19	0.720 72	9.874	0.069
Rb	37	0.705 25	10.55	0.064
Cs	55	0.699 41	11.42	0.061

[a]See Refs. 18 and 5.
[b]See Ref. 6.
[c]K. A. Gschneidner, Jr., Solid State Phys. **16**, 275 (1964).

pressure of these two metals could be determined. In particular, the theoretical zero-pressure densities were established. For the other alkali metals, however, no calculations were performed at lattice constants other than the experimental ones. Nevertheless, it is possible to estimate the errors in the zero-pressure densities that would be obtained for these other metals by comparing the theoretical pressures obtained at the experimental lattice constants with the experimentally known[22] compression curves. The percentage difference between the theoretical and experimental zero-pressure densities are given in the last column of Table I. These results can be compared with the experimental zero-pressure lattice constants and cohesive energies given in Table II.

The most striking features of the $\alpha = \alpha_{vt}$ results in Table I are the close agreement between experiment and theory for cesium and rubidium and the ordered decrease with respect to atomic number in the agreement for the other metals. It is significant that the lighter metals have calculated cohesive energies which are too great and theoretical zero-pressure lattice constants which are too small. Specifically, these results would seem to imply that the choice $\alpha = \alpha_{vt}$ overestimates the exchange correlation in the lighter alkali metals. If this conclusion is correct, then using an α less than α_{vt} should improve the results for the lighter alkali metals and degrade those of the heavier ones. The data given in the bottom-half of Table I appear to at least tentatively support this argument.

As has been mentioned earlier, the cohesion and pressure of lithium and cesium have been calculated at a number of different lattice constants. The results of these calculations are tabulated in Tables III and IV. For the purposes of locating the theoretical zero-pressure lattice constants and calculating the bulk moduli, it was found convenient to fit the computed cohesions of lithium and cesium to polynominals in the volume. In all cases, the highest-order polynominal possible was used; i.e., the order of the Lagrange polynominal in each instance was one less than the number of computed

TABLE III. Calculation of the cohesion and pressure of lithium.

Volume[a]	Cohesion (Ry)	P (virial theorem) (kbar)	$P\left(\dfrac{-dE}{dV}\right)$ (kbar)
110.72 $\alpha = \alpha_{vt}$	+0.149 213	+16.8	+17.0
116.30	+0.149 666	+7.0	+7.2
122.07	+0.149 779	−1.3	−1.1
131.07	+0.149 391	−11.2	−11.0
143.60	+0.148 024	−20.7	−20.6
131.07 $\alpha = \frac{2}{3}$	+0.123 125	+15.2	+15.2
137.31	+0.123 620	+8.1	+8.3
143.56	+0.123 842	+2.3	+2.4
150.38	+0.123 825	−3.0	−2.9

[a]Volume of the primitive unit cell in units of cubic atomic units.

points. The internal consistency of these calculations can be checked by comparing the pressures computed from these polynominals $(-dE/dV)$ with the pressures obtained by the virial theorem as has been done in the last two columns of Tables III and IV. It can be seen that the agreement between P (virial theorem) and P $(-dE/dV)$ is not nearly as good for the cesium data as it is for the lithium data. The cause of these small discrepancies in the cesium calculations is mainly the marginal adequacy with which the cesium compression curve can be fitted by a fifth-order polynominal.

In Table V, we give the computed zero-pressure cohesive energies, lattice constants, and bulk moduli of cesium and lithium and compare them with experimental values. As we would predict from Table I, an α of $\frac{2}{3}$ gives the best results for lithium, whereas for cesium, α_{vt} seems to be the more appropriate value to use.

TABLE IV. Calculation of the cohesion and pressure of cesium.

Volume[a]	Cohesion (Ry)	P (virial theorem) (kbar)	$P\left(\dfrac{-dE}{dV}\right)$ (kbar)
500.0 $\alpha = \alpha_{vt}$	+0.050 85	+14.5	+15.1
579.7	+0.057 00	+7.0	+8.1
665.5	+0.060 15	+2.7	+3.1
750.6	+0.061 05	−0.1	+0.2
976.6	+0.058 82	−3.0	−2.4
1230.2	+0.053 12	−3.9	−4.7
500.0 $\alpha = \frac{2}{3}$	+0.043 30	+17.7	+17.4
578.8	+0.050 60	+9.2	+10.2
665.5	+0.054 90	+4.3	+4.8
750.6	+0.056 60	+1.2	+1.4
976.6	+0.055 90	−2.1	−1.3
1314.0	+0.049 80	−3.4	−6.5

[a]Volume of the primitive unit cell in units of cubic atomic units.

TABLE V. Comparison of theoretical and experimental results for lithium and cesium.

		Cohesive energy (Ry)	Lattice constant (a.u.)	Bulk modulus (kbar)
Li	$X\alpha$ ($\alpha = 0.780\,87$)	0.150	6.2351	162
	Experiment	0.121[a]	6.5971[b]	123[c]
	$X\alpha$ ($\alpha = 0.666\,66$)	0.124	6.6403	115
Cs	$X\alpha$ ($\alpha = 0.699\,41$)	0.061	11.50	18
	Experiment	0.061[a]	11.42[b]	22[c]
	$X\alpha$ ($\alpha = 0.666\,66$)	0.057	11.75	14

[a]K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
[b]Reference 6.
[c]Reference 7.

Another point of interest is the contribution of each term in the total energy expression to the cohesive energy of the alkali metals. From Eqs. (1), (4), and (8), the cohesive energy can be written

$$C_{max} = \Delta T + \Delta U_c + \Delta U_{xc} , \qquad (9)$$

where

$$U_c = U_{en} + U_{nn} + U_{ee} . \qquad (10)$$

ΔT is the difference in the total kinetic energy per atom of the crystal and the total energy of the isolated atom. ΔU_c is the difference in the classical potential energies of the crystal and the atom, and ΔU_{xc} is the difference in the exchange-correlation potential energy of the crystal and the atom. In Table VI we have tabulated these differences for lithium and cesium at the two values of α. The entries in these tables have been obtained from Lagrange interpolating polynominals evaluated at the theoretical zero-pressure volumes. It is reassuring to see that within the computational accuracy the virial theorem is satisfied; i.e., $C_{max} = -\Delta T$. However, the most interesting aspect of Table VI is that it reveals the large role played by ΔU_{xc} in the binding of these metals. In particular, we see that for both lithium and cesium, ΔU_{xc} is larger than the cohesive energy. It is also interesting to note that ΔU_c is relatively insensitive to the choice

TABLE VI. Contributions of the total kinetic energy, the classical Coulomb energy, and the exchange-correlation energy to the cohesive energy of lithium and cesium.

	α	ΔT (Ry)	ΔU_c (Ry)	ΔU_{xc} (Ry)	Cohesive energy (Ry)
Li	0.780 87	−0.1493	+0.1142	+0.1850	+0.1499
	0.666 66	−0.1240	+0.1032	+0.1446	+0.1238
Cs	0.699 41	−0.0616	+0.0333	+0.0896	+0.0613
	0.666 66	−0.0550	+0.0328	+0.0793	+0.0571

of α, whereas ΔT and ΔU_{xc} are strongly affected. This last observation tends to support the notion that by reducing α, we are reducing the exchange-correlation energy contribution to the calculated cohesive energy of the alkali metals.

IV. DISCUSSION OF RESULTS

The results of Table I can perhaps be understood in terms of the following arguments. From the works of Schwarz[18] and Lindgren and Schwarz,[23] we know that the optimum α for an electron system is probably a functional of the electronic charge density.[24] In particular, we might suspect that as the lattice constant of an alkali metal is decreased from infinity, the value of the optimum α for the system should decrease. Of all the alkali metals, lithium has the largest cohesive energy, and, therefore, probably has a valence electronic charge density which differs most radically from the valence charge density of the isolated atom. Using an atomic optimized α in the lithium crystal is consequently not a particularly good approximation. Cesium on the other hand has a relatively small cohesive energy, and an atomic optimized α for such a solid is much more appropriate.

Several other workers[2,25] have done similar total energy calculations on lithium . The lithium calculation in the present paper is most easily compared with the work of Rudge. Using an α of $\frac{2}{3}$ and the muffin-tin approximation, Rudge obtained a theoretical lattice constant of 7.11 a.u., a cohesive energy of 0.084 Ry, and a bulk modulus of 109 kbar.[2] These results can be compared with those given in Table V. Although there are some minor differences between the calculation of Rudge and the one described here, it does not appear that they could be the source of the large discrepancies in the computed results for the cohesive energy and the equilibrium lattice constant. Liberman,[25] who has performed a somewhat similar bulk property calculation on lithium, obtained results which are in closer agreement with the $\alpha = \frac{2}{3}$ results in Table

V than they are with those of Rudge. Nevertheless, a satisfactory explanation of the disagreement between the results of Rudge and Table V is lacking.

It should be emphasized that only the bulk properties of the alkali metals near zero pressure have been considered in this work. Furthermore, the bulk properties of a solid essentially depend only upon the character of the valence electronic charge density. We should, therefore, be careful not to generalize these results to energy band calculations of other properties or to bulk property calculations in other solids. In particular, the present author does not at this point recommend the use of $\alpha = \frac{2}{3}$ in all energy-band calculations.

Another point worth making is that this calculation neglects both the corrections to the muffin-tin approximation and relativistic effects. From the works of Rudge[26] and Painter and Ellis,[27] we know that the non-muffin-tin contribution to the one-electron energies of lithium is less than about 0.005 Ry. Such a correction to the cohesive energy is not large enough to change the qualitative results for lithium but could possibly affect those of cesium. As for relativistic effects, there should be no problem with lithium but cesium is again a questionable case. In summary, it can be said that the results reported here for the lighter alkali metals are less likely to be severely different from relativistic non-muffin-tin calculations than are the results for the heavier elements.

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*Supported in part by the National Science Foundation.

[1]J. C. Slater and K. H. Johnson, Phys. Rev. B **5**, 844 (1972).

[2]W. E. Rudge, Phys. Rev. **181**, 1033 (1969).

[3]M. Ross and K. W. Johnson, Phys. Rev. B **2**, 4709 (1970).

[4]L. Kleinman and R. Shurtleff, Phys. Rev. B **4**, 3284 (1971).

[5]F. W. Averill, Phys. Rev. B **4**, 3315 (1971); see also J. B. Conklin, Jr., F. W. Averill, and T. M. Hattox, J. Phys. (Paris) (to be published).

[6]C. S. Barrett, Acta Cryst. **9**, 671 (1956).

[7]M. S. Anderson, E. J. Gutman, J. R. Packard, C. A. Swenson, J. Phys. Chem. Solids **30**, 1587 (1969).

[8]P. D. DeCicco, Ph.D. thesis (Massachusetts Institute of Technology, 1965) (unpublished).

[9]M. Ross, Phys. Rev. **179**, 612 (1969).

[10]J. C. Slater, *Advances in Quantum Chemistry* (Academic, New York, 1972), Vol. 6, p. 1.

[11]This procedure for summing over the states under the Fermi surface is the same as that of E. C. Snow and J. T. Waber [Phys. Rev. **157**, 570 (1967)].

[12]L. J. Sham, Phys. Rev. A **1**, 969 (1970).

[13]This observation concerning the relative merits of Eqs. (6) and (7) has been made many times before. See, for example, P. O. Löwdin, J. Mol. Spectry. **3**, 46 (1959).

[14]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[15]J. C. Slater, Phys. Rev. **51**, 846 (1937).

[16]For a discussion of the muffin-tin approximation to the total energy, see Ref. 3.

[17]This method of choosing an exchange factor was first suggested by M. Berrondo and O. Goscinski [Phys. Rev. 184, 10 (1969)].

[18]K. Schwarz, Phys. Rev. B 5, 2466 (1972).

[19]J. B. Mann, Los Alamos Scientific Laboratory Report No. LA-3690, 1967 (unpublished).

[20]W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[21]R. Gaspar, Acta Phys. Hung. 3, 263 (1954).

[22]C. A. Swenson, Phys. Rev. 99, 423 (1955).

[23]I. Lindgren and K. Schwarz, Phys. Rev. A 5, 542 (1972).

[24]This point has been previously made by Ross and Johnson (see Ref. 3).

[25]D. A. Liberman, Phys. Rev. B 3, 2081 (1971).

[26]W. E. Rudge, Phys. Rev. 181, 1024 (1969).

[27]D. E. Ellis and G. S. Painter, Phys. Rev. B 2, 2887 (1970).

Electron-Phonon Function $\alpha^2(\omega)F(\omega)$ for Thallium[*]

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A good deal of agreement is found to exist between the phonon spectrum derived from superconducting tunneling experiments and that obtained by inelastic-neutron-scattering data. However, some discrepancy has been observed in thallium. We discuss the reasons for these differences, and show how they can be largely eliminated by the proper choice of force constants and pseudopotentials.

I. INTRODUCTION

Inelastic neutron scattering yields the phonon dispersion curves in metals and other systems, usually along high-symmetry directions. These are fit by a Born–von Kármán force-constant model, which is then used to generate the phonon frequency distribution $F(\omega)$. For a strong-coupling superconductor, such as thallium, there exists an independent method of obtaining very much the same information. It is superconducting tunneling[1,2] on diodes involving strong coupling systems. In the current-voltage characteristics of such devices there exists an image of the phonons.

The I-V data can be "inverted" by the technique of McMillan and Rowell[1] to yield the electron-phonon function $\alpha^2(\omega)F(\omega)$. This function may be thought of as a product of some average electron-phonon coupling strength $\alpha^2(\omega)$ times the phonon frequency distribution $F(\omega)$. Inasmuch as the assumption that $\alpha^2(\omega)$ does not vary significantly with energy is valid, we obtain an independent measure of $F(\omega)$ which can be compared with neutron data.

A review of such comparisons has been made by Rowell and Dynes.[3] Generally, a considerable degree of agreement is obtained between these two techniques. At the moment, however, thallium appears to be an exception.

II. DISCUSSION

Worlton and Schmunk[4] (WS) have recently used neutron inelastic scattering to measure the thallium phonon dispersion curves along two high-symmetry directions at 77 and 296 °K. They analyzed their data in terms of the modified axially symmetric (MAS) force-constant model,[5] and used a least-squares-fitting procedure to derive the force constants. Since we are primarily interested in low-temperature calculations, we restrict our attention to their 77 °K results, for which WS present three force-constant models. We discuss model 1A[4] because its fit to experiment is as good or better than the other two models.

The dispersion curves as predicted by the WS model 1A are shown in Fig. 1, where we have used the lattice parameters[6] $a = 3.4496$ Å and $c = 5.5137$ Å. The labeling of the symmetry points along the horizontal axes follows the convention of Koster.[7] It is interesting to note that the more than linear increase in some of the acoustic modes, for small q, has been predicted by van der Hoeven and Keesom[8] on the basis of specific-heat measurements in thallium.

The density of phonon states is

$$F(\omega) = \frac{V}{N} \int_{\mathrm{FBZ}} \frac{d^3q}{(2\pi)^3} \sum_j \delta\left(\omega - \omega_j(\vec{q})\right), \qquad (1)$$

where V is the total crystal volume and N is the number of unit cells. The integration is over the first Brillouin zone (FBZ) and the sum on j extends over six phonon branches. The phonon frequency of the $(\vec{q}j)$th mode is $\omega_j(\vec{q})$; and the normalization condition $\int_0^\infty d\omega\, F(\omega) = 6$ applies.

The frequency distribution $F(\omega)$, calculated using the 1A model, is shown in Fig. 2 by the dashed line. The I-V characteristics of thallium have been measured,[9,10] and the dots in this figure