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Nonlocal pseudopotential calculation of lattice-dynamical properties of cesium metal

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The phonon dispersion relations $\omega(\mathbf{q})$ are calculated for cesium metal with use of a refined version of the Harrison first-principles nonlocal pseudopotential formalism. Consistent with previous work for the other alkali metals, the Lindgren exchange with orthogonalized plane-wave functions for the conduction-electron density has been used in the present calculations. The Grüneisen parameter γ, which is obtained from the calculated $\omega(\mathbf{q})$, is in agreement with experimental values to within 10%. The elastic shear constants, $C_{11}-C_{12}$ and C_{44}, have also been computed and compare well with measured values. Using the energy-wave-number characteristic evaluated for the liquid density, the static structure factor and electronic transport properties of liquid cesium have also been computed and found to be in good agreement with experimental data. The agreement provides a confirmation of the theoretical phonon spectra $\omega(\mathbf{q})$ for cesium, albeit indirectly. The computed $\omega(\mathbf{q})$ also compare well with other theoretical results and recently reported experimental measurements on polycrystalline cesium.

I. INTRODUCTION

Experimental and theoretical phonon dispersion relations $\omega(\mathbf{q})$ have been obtained for most of the alkali metals during the past two decades.[1-8] However, the phonon spectra for the heaviest alkali metal, Cs, have still not been measured experimentally from single-crystal faces even though several theoretical calculations[9-11] have been done. Specifically, theoretical determinations of $\omega(\mathbf{q})$ for Cs have been made by Ho,[9] by Ramamurthy and Sakshkumar[10] and by Taylor and MacDonald.[11] The first two groups have used experimental data for the elastic constants to adjust the model-potential parameters. Taylor and MacDonald have done a nonlocal pseudopotential calculation of $\omega(\mathbf{q})$ for Cs. In their procedure the pseudopotential parameters are chosen so that the pseudopotential can reproduce the nonlinear electron charge density accurately outside the ion core. Most recently, Nücker and Buchenau[12] have reported, for the first time, neutron scattering studies of phonon spectra for polycrystalline samples of Cs using the time-of-flight method.

In this paper we report the calculation of phonon spectra of Cs metal using a refined version of the Harrison[13] first-principles pseudopotential formalism. In this procedure, the pseudopotential is constructed strictly from fundamental atomic properties such as the atomic number and atomic mass, the lattice constant, and the wave functions and eigenenergies of core electrons for the isolated ion. The formalism we have used includes (i) a more exact form of V_{OPW},[14,15] (ii) the Lindgren[16] conduction-core exchange with orthogonalized plane waves (OPW's) for the conduction electrons,[17] and (iii) the Singwi-Sjolander-Tosi-Land[18] (SSTL) dielectric screening function. We have previously used the same modified scheme of the Harrison theory in a systematic study of the lattice-dynamical properties of the other alkali metals, Li, Na, K, and Rb.[17,19,20] In all cases the calculated results have been in good to excellent agreement with experiments.

We have already reported the calculation of the Grüneisen parameter[21] which has been evaluated using the phonon spectra obtained in the present work. The computed overall Grüneisen parameter γ is found to be in good agreement (i.e., within 10%) with experiment.[22] The calculated mode-Grüneisen parameters $\gamma(\mathbf{q},s)$ also exhibit the typical curves for alkali metals.[23] Here, γ is obtained by taking an average of $\gamma(\mathbf{q},s)$ over wave vector $\mathbf{q}$ and mode s. The $\gamma(\mathbf{q},s)$ represents the volume dependence of $\omega(\mathbf{q})$ for each mode within the quasiharmonic approximation. In addition, the theoretical elastic shear constants $C_{11}-C_{12}$ and C_{44} are found to agree within 20% with experimental data, where the same energy-wave-number characteristic $F(q)$ is used as in the phonon calculations. The agreement represents a confirmation of the theoretical phonon dispersion relations of the Cs metal, albeit indirectly.

The same pseudopotential formalism has also been used in the calculations of the static structure factor $S(q)$, electrical resistivity ρ, and thermopower Q_T of liquid Cs metal[24] by evaluating the pseudopotential at the melting point. Although the computed ρ differs from the experimental value by a factor of 2, the calculated $S(q)$ and Q_T have been found to be in excellent agreement with experiment.[25,26] The static structure factor $S(q)$ has been calculated using a Monte Carlo simulation of the liquid Cs metal. The same procedure has been used to yield good structure factors for the other alkali metals.[19,20] The effective ion-ion pair potential used in the simulation is obtained from the same pseudopotential that yields the form factor. Therefore, both the structure factor and the form factor are used "self-consistently" in the Ziman formula[27] for ρ and Q_T. We have argued that the discrepancy of ρ can be attributed to inadequacies of the free-electron approximation in the Ziman theory rather than the Harrison pseudopotential formalism. This has been discussed in more detail elsewhere in the literature.[24]

In Sec. II, we outline the first-principles nonlocal pseudopotential formalism. The theory of lattice dynamics appropriate for cesium is briefly given in Sec. III. The details of the calculations and the results for the phonon dispersion curves, elastic shear constants, and Grüneisen parameters are given in Sec. IV.

II. HARRISON FIRST-PRINCIPLE PSEUDOPOTENTIAL

In the Harrison[13] formalism the second-order perturbation term due to the ion-electron interaction (i.e., pseudopotential) is the structure-dependent band energy E_{BS}. This is written as

$$E_{\mathrm{BS}}=\sum_{\mathbf{q}\neq 0} |S(\mathbf{q})|^2 F(|\mathbf{q}|) , \tag{1}$$

where $S(\mathbf{q})$ is the geometrical structure factor and $F(q)$ the energy-wave-number characteristic. The function $F(q)$ is given by

$$F(q)=\frac{2\Omega_0}{(2\pi)^3}\int d^3k \frac{|\langle \mathbf{k}+\mathbf{q} | W | \mathbf{k}\rangle|^2}{(\hbar^2/2M)(k^2-|\mathbf{k}+\mathbf{q}|^2)} - \frac{\Omega_0 q^2}{8\pi e^2}\frac{|\langle \mathbf{k}+\mathbf{q} | W^{\mathrm{sc}} | \mathbf{k}\rangle|^2}{1-G(q)} , \tag{2}$$

where Ω_0 is the volume per ion, W the pseudopotential, and $|\mathbf{k}\rangle$ the normalized plane wave for a conduction electron of wave number $\mathbf{k}$. The second term on the right-hand side of Eq. (2) is a correction due to counting the electron-electron interaction twice in the self-consistent field approximation. The function $G(q)$ is introduced to account for the screening effect of the conduction electrons.[28]

The matrix element of the pseudopotential W is given by

$$\langle \mathbf{k}+\mathbf{q} | W | \mathbf{k}\rangle = \langle \mathbf{k}+\mathbf{q} | V^c | \mathbf{k}\rangle + \langle \mathbf{k}+\mathbf{q} | W^R | \mathbf{k}\rangle + \langle \mathbf{k}+\mathbf{q} | W^{\mathrm{sc}} | \mathbf{k}\rangle , \tag{3}$$

where V^c is the crystal potential, W^R the repulsive potential, and W^{sc} the screening of V^c and W^R. The first two terms are usually called the bare potential matrix elements in contrast to the screening potential matrix element.

$V^c(r)$ is the Coulomb potential arising from the nucleus and the charge distribution of core and conduction electrons. In general, the crystal potential V^c has the following contributions: (i) the potential due to the single ion (i.e., nucleus plus core electrons), (ii) the conduction-band—core exchange, (iii) the correlation between conduction and core electrons, and (iv) the potential due to the charge density of single-OPW states of the conduction electron.

W^R is the positive potential that results from the orthogonalization of conduction states to core states. The matrix element of W^R is given by

$$\langle \mathbf{k}+\mathbf{q} | W^R | \mathbf{k}\rangle = \sum_{n,l}\left[\frac{\hbar^2 k^2}{2m}+\langle \mathbf{k} | V^c | \mathbf{k}\rangle - E_{nl}\right]\langle \mathbf{k}+\mathbf{q} | nl\rangle\langle nl | \mathbf{k}\rangle + \sum_{n,l}\left[\frac{\hbar^2 k^2}{2m}+\langle \mathbf{k} | V^c | \mathbf{k}\rangle - E_{nl}\right]\langle \mathbf{k} | nl\rangle\langle nl | \mathbf{k}\rangle \frac{\langle \mathbf{k}+\mathbf{q} | p | \mathbf{k}\rangle}{1-\langle \mathbf{k} | p | \mathbf{k}\rangle} , \tag{4}$$

where E_{nl} and $|nl\rangle$ are the eigenvalues and eigenfunctions of the core electrons for an ion in a metal, respectively, and m is the electron mass. P, given by $P=\sum_{n,l}|nl\rangle\langle nl|$, is the projection operator onto the core states. Here, the $|nl\rangle$ represent the core-electron states for an isolated ion as well as those for a bound ion in a metal. Both values are considered to be the same in the small-core approximation, which is essential in the Harrison pseudopotential scheme.

In the fully nonlocal theory, the screening of W^R is considered along with the screening of V^c. Therefore, the matrix element of W^{sc} is the sum of two contributions:

$$\langle \mathbf{k}+\mathbf{q} | W^{\mathrm{sc}} | \mathbf{q}\rangle = \frac{1-\epsilon(q)}{\epsilon(q)}\langle \mathbf{k}+\mathbf{q} | V^c | \mathbf{k}\rangle + \frac{2e^2[1-G(q)]}{\pi^2\epsilon(q)q^2}\int d^3k \frac{\langle \mathbf{k}+\mathbf{q} | W^R | \mathbf{k}\rangle}{(\hbar^2k^2/2M)(k^2-|\mathbf{k}+\mathbf{q}|^2)} , \tag{5}$$

where $\epsilon(q)$ is the dielectric response function for the interacting conduction electron gas. It is given by

$$\epsilon(q)=1+[1-G(q)][\epsilon^H(q)-1] , \tag{6}$$

where $\epsilon^H(q)$ is the free-electron or Hartree dielectric constant. The SSTL screening function[18] is used because it satisfies the compressibility sum rule and yields reasonable values of the pair correlation function for small r, the interionic separation.

In the Harrison scheme, it is assumed that the eigenvalues of the core states for the isolated ions may be slightly shifted (i.e., core shift) in the metallic state, but the wave functions do not undergo any significant change. In this first-order approximation, the core shift V_{OPW} is given by the potential energy of the core electron under the orthogonalization-hole

(OH) charge field. The OH can be interpreted as a depletion of core-electron charge density. Cutler *et al.*[14] derived the exact expression of the OH charge density $n_{\text{OH}}(r)$; this is given by

$$n_{\text{OH}}(r)=\frac{4\Omega_0}{(2\pi)^3}\int_0^{k_F}k^2dk\sum_{n,l}\frac{(2l+1)\langle\mathbf{k}\,|\,nl\rangle P_{nl}(r)}{r}\left[\left[\frac{4\pi}{\Omega_0}\right]^{1/2}j_1(kr)-\sum_{n'}\frac{P_{n'l}(r)\langle\mathbf{k}\,|\,n'l\rangle}{2r}\right], \tag{7}$$

where $P_{nl}(r)$ is the radial wave function and $j_1(kr)$ the spherical Bessel function. In addition to the core shift, another explicit change due to the OH is the effective valence Z^*:

$$Z^*=Z+\frac{1}{N}\sum_{k<k_F}\frac{\langle\mathbf{k}\,|\,P\,|\,\mathbf{k}\rangle}{1-\langle\mathbf{k}\,|\,P\,|\,\mathbf{k}\rangle}, \tag{8}$$

where N is the number of ions. The effective valence Z^* is used in the calculation of the effective ion-ion pair potential for the phonon frequencies, the elastic constants of the solid, and in the Monte Carlo simulation for the static structure factor of the liquid metal.

The Lindgren approximation[16] of the conduction-core exchange interaction is given by

$$V^L(r)=-3e^2\left[\frac{3}{8\pi}\right]^{1/2}\{[\rho_{\text{core}}(r)+\rho_{\text{cond}}(r)]^{1/3}-[\rho_{\text{cond}}(r)]^{1/3}\}, \tag{9}$$

where $\rho_{\text{cond}}(r)$ and $\rho_{\text{cond}}(r)$ are the core- and conduction-electron charge density, respectively.

The subtraction of the conduction-conduction exchange $\rho_{\text{cond}}^{1/3}(r)$ in the Lindgren form yields an asymptotic behavior of the conduction-core exchange near the cell boundary such that $V^L(r)\approx 0$, as is physically required. Thus, the Lindgren approximation should, in general, lead to a better representation of the conduction-core exchange than the Slater[29] or the Kohn-Sham[30] approximation. Within this approximation, we do not explicitly treat the core-core exchange because its effect is already included in the calculation of core states.

The use of the OPW conduction states in the Lindgren exchange approximation has systematically improved the pseudopotential calculations of lattice-dynamical properties for the alkali metals.[17,19] The OPW state is given by

$$|\,\mathbf{k}\rangle_{\text{OPW}}=(1-\langle\mathbf{k}\,|\,P\,|\,\mathbf{k}\rangle)^{-1/2}(1-P)\,|\,\mathbf{k}\rangle, \tag{10}$$

where $(1-\langle\mathbf{k}\,|\,P\,|\,\mathbf{k}\rangle)^{-1/2}$ is the normalization factor. Squaring $|\,\mathbf{k}\rangle_{\text{OPW}}$, the conduction-electron charge density can be written as a sum of uniform and localized charge densities:

$$\rho_{\text{cond}}(r)=\Omega_0^{-1}(1-\langle\mathbf{k}\,|\,P\,|\,\mathbf{k}\rangle)^{-1}+n_{\text{OH}}(r). \tag{11}$$

The first term is the constant charge density and can be interpreted as the effective valence $(1-\langle\mathbf{k}\,|\,P\,|\,\mathbf{k}\rangle)^{-1}$ uniformly distributed over the volume Ω_0. In fact, the factor $(1-\langle\mathbf{k}\,|\,P\,|\,\mathbf{k}\rangle)^{-1}$ is approximately equal to the effective valence Z^*. The second term is the OH charge density localized at each ion site, and is given by Eq. (7).

III. THEORY OF LATTICE DYNAMICS FOR CESIUM

In the Born—von Kármán[31] theory, the phonon frequencies are given by the solutions of the secular equations,

$$|\,\tilde{D}(\mathbf{q})-M\omega^2(\mathbf{q})\tilde{1}\,|=0, \tag{12}$$

where $\tilde{D}(\mathbf{q})$ is the dynamical matrix, $\tilde{1}$ the unit matrix, and M the mass of the ion. In general, the 3×3 matrix $\tilde{D}(\mathbf{q})$ is written as the sum of three contributions:

$$\tilde{D}(\mathbf{q})=\tilde{D}^{C}(\mathbf{q})+\tilde{D}^{E}(\mathbf{q})+\tilde{D}^{R}(\mathbf{q}). \tag{13}$$

Here, $\tilde{D}^{C}(\mathbf{q})$ is the Coulombic or Ewald contribution due to the direct electrostatic interaction between point ions. $\tilde{D}^{E}(\mathbf{q})$ is the electron or band-structure contribution due to the electron-ion interaction. $\tilde{D}^{R}(\mathbf{q})$ is a repulsive contribution due to the overlap between the closed shells of the ions, which is negligible in the small-core approximation. This approximation may be questionable for the heavier alkali metals Rb and Cs. Nevertheless, it is used here to be consistent with our systematic treatment of all the contributions to the pseudopotential for the other alkali metals.

The Coulombic term can be computed by considering a lattice of point ions immersed in a uniform compensating background of negative charge. Derivations of $\tilde{D}^{C}(\mathbf{q})$ have been given by Ewald[32] and Thompson.[33] The results can be written in the following form:

$$\begin{aligned}\tilde{D}^{C}(\mathbf{q})=&\frac{4\pi(Z^*e)^2}{M\Omega_0}\sum_{\mathbf{G}\neq0}\left[\frac{(\mathbf{G}+\mathbf{q})(\mathbf{G}+\mathbf{q})}{|\,\mathbf{G}+\mathbf{q}\,|^2}e^{-|\mathbf{G}+\mathbf{q}|^2/4\eta^2}-\frac{\mathbf{G}\mathbf{G}}{G^2}e^{-G^2/4\eta^2}\right]\\&+\frac{(Z^*e)^2}{M}\sum_{\mathbf{X}\neq0}\left[\frac{\mathbf{X}\mathbf{X}}{X^2}\left[\frac{3\,\text{erfc}(\eta X)}{X^3}+\frac{6\eta e^{-\eta^2X^2}}{\sqrt{\pi}X^2}+\frac{4\eta^3e^{-\eta^2X^2}}{\sqrt{\pi}}\right]-\tilde{1}\left[\frac{2\eta e^{-\eta^2X^2}}{\sqrt{\pi}X^2}+\frac{\text{erfc}(\eta X)}{X^3}\right]\right](1-e^{-i\mathbf{q}\cdot\mathbf{X}}),\end{aligned} \tag{14}$$

where erfc(x) is the complementary error function, and $\mathbf{G}$ and $\mathbf{X}$ are the reciprocal and real lattice vectors, respectively. The parameter η is chosen to make both the sums over $\mathbf{G}$ and $\mathbf{X}$ converge rapidly.

The electronic term can be regarded as the difference between band-structure energies of a perturbed lattice and a lattice in equilibrium. By expanding the structure factor $S(\mathbf{q})$ in Eq. (1), we easily obtain $\tilde{D}^{E}(\mathbf{q})$,

$$\tilde{D}^{E}(\mathbf{q})=\frac{2}{M}\sum_{\mathbf{G}\neq 0}[(\mathbf{G}+\mathbf{q})(\mathbf{G}+\mathbf{q})F(|\mathbf{G}+\mathbf{q}|)-\mathbf{G}\mathbf{G}F(|\mathbf{G}|)] . \tag{15}$$

This equation provides the connection between the pseudopotential and the phonon dispersion relation $\omega(\mathbf{q})$ through the energy-wave-number characteristic $F(q)$, given by Eq. (2).

In the quasiharmonic approximation the mode-Grüneisen parameter $\gamma(\mathbf{q},s)$ is defined by

$$\gamma(\mathbf{q},s)=-\frac{d\ln\omega(\mathbf{q},s)}{d\ln\Omega} , \tag{16}$$

where s refers to the mode. The overall Grüneisen parameter γ is the average of $\gamma(\mathbf{q},s)$ with the mode specific heat as the weighting factor,

$$\gamma=\frac{\sum_{\mathbf{q},s}\gamma(\mathbf{q},s)C_v(\mathbf{q},s)}{\sum_{\mathbf{q},s}C_v(\mathbf{q},s)} , \tag{17}$$

where $C_v(\mathbf{q},s)$ is the contribution of the mode $(\mathbf{q},s)$ to the specific heat at constant volume, $C_v=\sum_{\mathbf{q},s}C_v(\mathbf{q},s)$.

The elastic shear constants are related to the elastic energy density Φ by the following equations:

$$\left[\frac{\partial^2\Phi}{\partial\epsilon_1^2}\right]_0=\tfrac{3}{2}(C_{11}-C_{12}) \tag{18}$$

$$\left[\frac{\partial^2\Phi}{\partial\epsilon_2^2}\right]_0=3C_{44} , \tag{19}$$

where subscript 0 refers to the equilibrium displacement and ϵ_1 and ϵ_2 are the deformation parameters related to the strains. Similar to the calculation of the phonon dispersion relation, an electrostatic and an electronic term are the two main contributions to Φ. The repulsive term is also neglected here as in the calculation for $\omega(\mathbf{q})$. We do not consider the contribution from the free-electron gas since its energy depends only on the volume and the elastic shear constants are independent of the volume charge.

IV. CALCULATIONS AND RESULTS

The Herman-Skillman atomic program[34] is used to obtain the eigenenergies ε_{nl} and wave functions $|nl\rangle$ of the core electrons for an isolated Cs ion. The set of ε_{nl} and $|nl\rangle$ are used to evaluate the energy-wave-number characteristic $F(q)$ (see Fig. 1). As shown in Table I, theoretical values of ε_{5s} and ε_{5p} are somewhat smaller than the corresponding experimental data,[35] i.e., the second and third ionization energies of atomic Cs, respectively. This discrepancy represents a consistent pattern for all calculated energies of the alkali elements in the use of the Herman-Skillman program for the Hartree-Fock-Slater theory. Nevertheless, these energies and wave functions have yielded good phonon dispersion relations for the other alkali metals, Li, Na, K, and Rb.[17,19]

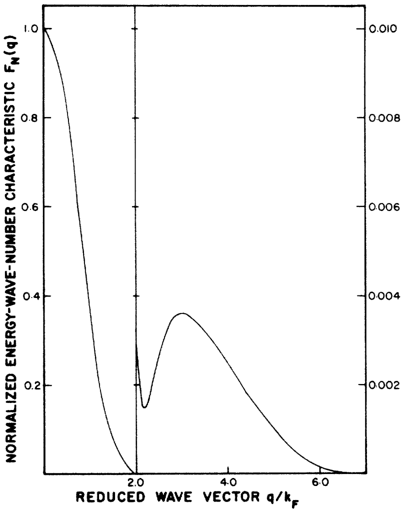

FIG. 1. Normalized energy-wave-number characteristic $F_N(q)$ for Cs metal at 5 K: $F_N(q)=[2\pi(Z^*e)^2/q^2\Omega_0]^{-1}F(q)$. The normalized factor is the asymptotic form of $F(q)$ in the limit as $q\to 0$. The experimental values used as input are the mass $M=132.9054$ amu and the lattice constant $a=6.045$ Å.

The experimental values used in the calculation of $F(q)$ are the atomic mass of $M=132.9054$ and the lattice constant $a=6.045$ Å.[36] The latter value implies that evaluation of lattice-dynamical properties for the solid Cs are made at 5 K. We have used the two lattice parameters $a=6.045$ and 6.050 Å to compute the mode-Grüneisen parameter $\gamma(\mathbf{q},s)$ given by Eq. (16). The effective valence Z^* is theoretically obtained from Eq. (8) and found to be 1.248.

The phonon dispersion curves, obtained by solving Eq. (12), are shown in Fig. 2. No noticeable difference is found between the use of 40 or 80 mesh points in the first Brillouin zone. Some mesh dependence was observed in the region close to the Γ point. However, this implies only the sensitivity of the numerical treatment for evaluating Eqs. (2) and (5) for small q around the singular point. Thus, all contributions to the dynamical matrix are computed accurately by summing over 300 real-space vectors and 500 reciprocal vectors. Convergence is found to be satisfactory with the choice of $\eta=(4/\Omega_0)^{1/3}$ in Eq. (14). This value of η has also been used for all the other alkali-metal phonon calculations. In the present calculations, the quasiharmonic approximation is assumed valid at 5 K so that the cubic and the higher-order anharmonic

TABLE I. Eigenenergies ε_{nl} of a Cs ion calculated using the Herman-Skillman program for the Hartree-Fock-Slater theory (in Ry).

n/l	s	p	d
1	−2531.270		
2	−389.863	−368.373	
3	−82.273	−72.970	−55.506
4	−16.161	−12.757	−6.806
5	−2.487 (−2.574)[a]	−1.619 (−1.846)[a]	

[a] The second and third ionization energies of the Cs atom (Ref. 35).

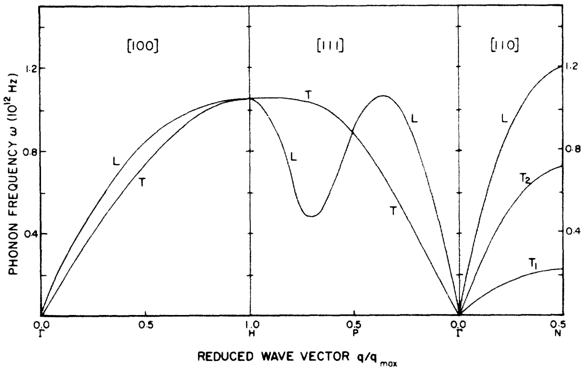

FIG. 2. Phonon dispersion curves for Cs metal at 5 K. The effective valence of $Z^*=1.248$ is used as the ionicity of the ion. This is the theoretical value which is obtained from Eq. (8). Comparison with other theoretical results and experimental data of $\omega(\mathbf{q})$ for polycrystalline cesium is made at symmetry points in Table II. Theoretical results are obtained for a single crystal.

terms can be neglected.

In Table II, this calculation is compared with other theoretical results for the phonon spectra of Cs. The comparison, made at the symmetry points, is seen to give good to excellent agreement. Taylor *et al.*[11] have constructed their pseudopotential so that the nonlinear charge density outside the core region is accurately reproduced. Using the pseudoatom technique, Moriarty[37] has considered *s*-*d* hybridization in the lattice-dynamical properties for Rb and Cs metals even though his values are limited to the high-symmetry points. In the present scheme, we have not included the *s*-*d* mixing contribution because of complications in its evaluation. However, Moriarty's results show that this contribution is not significant for $\omega(\mathbf{q})$ even in Cs. In Fig. 3 comparison is made between the effective ion-ion pair potentials for the present scheme and that of Taylor and MacDonald.[11,38] The present calculations predict a nearest-neighbor distance of 5.8 Å which compares well with the observed first-nearest-neighbor distance of 5.4 Å for Cs metal.[36]

The phonon spectra for polycrystalline cesium have recently been obtained for the first time.[12] These are compared with our theoretical results in Table II. The measured values of $\omega(\mathbf{q})$ at symmetry points are systematically lower than the theoretical ones obtained for a single crystal. These differences reflect the effect of random scattering in the polycrystalline material which both reduces the intensity of $\omega(\mathbf{q})$ and broadens the peak. Allowing these differences between the polycrystalline and single-crystal samples, the current calculations, as well as the other theoretical phonon spectra,[11,37] can be considered to be in equally good agreement with the experimental data.

TABLE II. Theoretical phonon frequencies $\omega(\mathbf{q})$ for Cs metal (in 10^{12} Hz).

	L(100)	L(110)	T(110)	T(110)
Present	1.06	1.20	0.23	0.72
Taylor[a]	1.03	1.20	0.24	0.71
Moriarty[b]	1.06	1.27	0.22	0.69
Moriarty[c]	1.09	1.29	0.21	0.70
Experiment[d]	0.96	1.07	0.22	0.63

[a] Reference 11.

[b] Pseudoatom model calculation without *s*-*d* hybridization (Ref. 37).

[c] Pseudoatom model calculation with *s*-*d* hybridization (Ref. 37).

[d] Inelastic neutron phonon spectra measured for polycrystalline Cs at 50 K (Ref. 12).

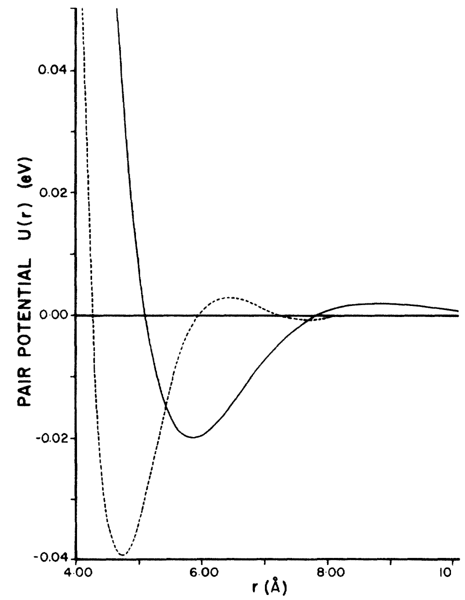

FIG. 3. Effective ion-ion pair potentials $U(r)$ at 5 K for the present scheme (solid line) and Taylor's (dashed line) (Refs. 11 and 38). $U(r)$ is given by

$$U(r)=\frac{(Z^*e)^2}{r}+\frac{2\Omega_0}{(2\pi)^3}\int F(q)e^{i\mathbf{q}\cdot\mathbf{r}}d^3q\ .$$

The first-nearest-neighbor distance is 5.4 Å for a bcc crystal of cesium.

Although indirect, additional verifications for the theoretical phonon dispersion relations of Cs are provided by the agreement between experimental and theoretical values of Grüneisen parameter and elastic constants[21] for the crystalline Cs. The overall Grüneisen parameter obtained from Eq. (16) agrees well with experiment: $\gamma_{\text{theor}}=1.20$ (5 K) and $\gamma_{\text{expt}}=1.28$ (90 K) and 1.16 (293 K).[22] The elastic shear constants are also in good agreement with experiment. Theoretical values of $C_{11}-C_{12}$ and C_{44} at 5 K are 0.033 and 0.181, respectively, while the corresponding experimental values[39] at 4.2 K are 0.041 and 0.160, in units of 10^{11} dyn/cm^2. We note that the calculation of the Grüneisen parameters and the elastic constants were computed using the same $F(q)$ as in the calculation of the phonon dispersion relations.

The calculated liquid-metal properties[24] provide further confirmation of the pseudopotential. The static structure factor $S(q)$ was obtained via a Monte Carlo simulation and found to be in very good agreement with experimental results. A noticeable improvement was obtained in the values of the thermopower Q_T and electrical resistivity at the melting point; $Q_T^{\text{theor}}=5.51$, $Q_T^{\text{expt}}=6.5$ μV/K,[26] and $\rho_{\text{theor}}=18.2$, $\rho_{\text{expt}}=36$ $\mu\Omega$ cm.[40] It is stressed that the same form of pseudopotential was used for the calculation of the lattice-dynamical and liquid-metal properties. That is, there is no distinction in the formulation of or contribution to $F(q)$ other than the effects due to temperature.

It is well known that nonlocality is important in pseudopotential calculations of solid and liquid metal properties. In the present scheme, nonlocality is manifested by the explicit $\mathbf{k}$ dependence of the pseudopotential matrix element $\langle \mathbf{k}+\mathbf{q} | W | \mathbf{k} \rangle$. In general, the local pseudopotential scheme neglects the $\mathbf{k}$ dependence by (usually) taking a simple analytical form of the ion-electron interaction. Nevertheless, this does not necessarily lead to more reliable results.

Sun *et al.*[17] and Day *et al.*[41] have stated that a nonlocal pseudopotential will often yield significant differences in the calculated physical properties as compared to those calculated with a local pseudopotential. In particular, Day *et al.* have shown that the use of a local approximation results in a considerable change in the phonon spectra when compared to a nonlocal calculation, even for so simple a metal as Na. Young and Ross[42] have also discussed the importance of the nonlocal treatment of a pseudopotential in obtaining reasonable values of the Grüneisen parameters γ at high pressure. They have found that their local pseudopotential treatment led to negative values of γ at high pressure for Na and K, which are physically unacceptable.

Among the contributions to the pseudopotential, the conduction-core exchange is the most dominant term after the ionic Coulomb potential. Moreover, it has been found that an accurate treatment of the exchange is necessary to obtain consistently good results in systematic calculations of lattice-dynamical properties. Thus, for all the alkali metals, the Lindgren[16] form of the conduction-band—core exchange is used with OPW's for the conduction-band states. As seen in Eq. (11), the OPW contribution is obtained by simply adding the $n_{\mathrm{OH}}(r)$ to be the constant value for the conduction-electron charge density. Sun *et al.* have previously used this technique to obtain a significant improvement in lattice-dynamical and liquid-metal properties of Rb. The use of the Lindgren exchange in the present calculations for Cs exhibits the same consistent improved behavior of $\omega(\mathbf{q})$ as for Rb.

Calculation indicates that the conduction-core correlation is not a major factor in determining the phonon dispersion relation $\omega(\mathbf{q})$. In the present work the Pines[43] form is used. OPW's were used for the conduction states in the Pines correlation function. This did not yield any noticeable difference in either the phonon spectra of the Grüneisen parameter when compared with the results for plane waves.

Three different form of $G(q)$, the SSTL, the Kleinman-Langreth (KL),[44] and the Overhauser (OV),[45] were used to investigate the screening effect in the lattice dynamics. Among the screening functions considered in the literature,[28] the KL and the OV forms are classified as the strongest and the intermediate screening, respectively, while the SSTL lies between the two in strength. The dispersion relations $\omega(\mathbf{q})$ show only small changes with the use of different forms of screening; specifically, the height of the $\omega(\mathbf{q})$ curve is 2% lower for the KL and 2% higher for the OV, compared to the SSTL. Neither the KL nor the OV gives better agreement with the experimental Grüneisen parameters than the SSTL screening function.

In conclusion, the phonon dispersion relations and other lattice-dynamical properties of cesium metal have been calculated using a refined version of the Harrison *a priori* pseudopotential formalism. The same pseudopotential scheme has been used to obtain good to excellent results for both lattice-dynamical and liquid-state properties of the other alkali metals, Li, Na, K, and Rb. In the present work, the phonon dispersion curves are in excellent agreement with other first-principles pseudopotential results. In addition, experimental verification for the theoretical phonon dispersion curves of cesium is provided, albeit indirectly, by the agreement between the computed and experimental values of the elastic shear constants and the Grüneisen parameters for cesium metal. We have also found that the calculated properties of liquid cesium are in good agreement with the experimental structure factor and electrical transport parameters, providing further confirmation of the nonlocal pseudopotential for cesium. The present calculations are also found to be consistent with the experimental phonon spectra for polycrystalline cesium reported very recently. These results strongly suggest the accuracy of the refined Harrison pseudopotential formalism for treating lattice-dynamical and liquid-metal properties of the alkali metals.

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