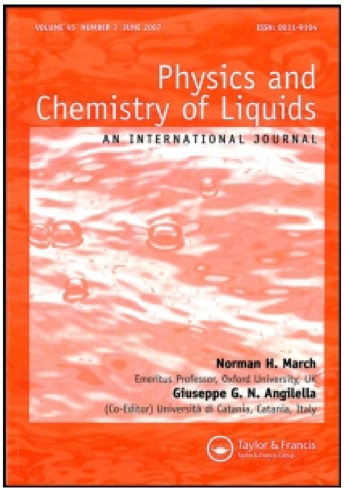

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Moon S. Chung[a]; Paul H. Cutler[a]; Franklin Sun[b]
[a] Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, USA [b] Irex Corporation, Ramsey, New Jersey, USA

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Nonlocal Pseudopotential Calculations of the Structure Factor and Electronic Transport Properties of Liquid Cesium†

MOON S. CHUNG, PAUL H. CUTLER
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

and

FRANKLIN SUN
Irex Corporation, 69 Spring Street, Ramsey, New Jersey 07446, USA

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A first-principles nonlocal pseudopotential formalism is used to calculate the effective ion–ion pair potential $U(r)$ for liquid cesium at the melting point (28.4°C). The potential $U(r)$ is then used in a Monte Carlo simulation to obtain the pair correlation function $g(r)$. The static structure factor $S(q)$ is calculated using the Fourier transformation of $g(r)$ for $q > 0.6(\text{a.u.})^{-1}$ and Fowler's formula for $q < 0.6(\text{a.u.})^{-1}$ and compared with X-ray and neutron scattering data. Good overall agreement is found between the calculated $S(q)$ and the experimental X-ray curve. In addition, the isothermal compressibility limit is satisfied at low q. The first-principles pseudopotential form factor and $S(q)$ are used self-consistently in Ziman's theory to calculate the electrical resistivity, ρ, and thermoelectric power Q. Although ρ differs by a factor 2 with experimental data at 30°C, the Q agrees with experiment in magnitude as well as sign. A possible explanation is given for the discrepancy in ρ.

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I INTRODUCTION

In this paper we report the calculation of the static structure factor and the electronic transport properties of liquid cesium using a refined version of the Harrison[1] first principle nonlocal pseudopotential theory. The formalism we have used includes (i) a more exact form of V_{OPW},[2,3] (ii) the Lindgren[4] conduction-core exchange with OPW's for the conduction electron density, and (iii) the SSTL[5] dielectric screening function to calculate the effective ion–ion pair potential $U(r)$. We have previously used the same modified form of the Harrison theory in a systematic study of similar properties of the other liquid alkali metals, Li, Na, K and Rb.[6–8] In almost all instances the calculated properties of these metals have shown good to excellent agreement with experiment.

Prior to the determination of the liquid Cs properties, this formalism is used in the calculation of the lattice dynamical properties of the crystalline phase of Cs metal. Using the pseudopotential matrix element $\langle \mathbf{k} | W | \mathbf{k} + \mathbf{q} \rangle$ evaluated at 5°K, we obtained the phonon dispersion relations,[9] elastic shear constants and Grüneisen parameters[10] for crystalline Cs. Although no experimental data are yet available for comparison, the calculated phonon dispersion curves are in excellent agreement with those obtained in the first-principles pseudopotential calculation of Taylor *et al.*[11] In addition, good agreement is found between the calculated and experimental values of the elastic shear constants and Grüneisen parameters of Cs. The latter agreement confirms, albeit indirectly, the theoretical phonon spectra for Cs metal.

In computing the properties of liquid Cs metal, a Monte Carlo (MC)[12] simulation was used to generate a large number of configurations of the liquid. The pair correlation function $g(r)$, was first determined. However, in the larger-r region the asymptotic form of $g(r)$[13] was used instead of the MC numerical determination of $g(r)$. This is done to avoid an excessively large number of simulations. A more detailed justification for this replacement is given in Section III. We next calculated the static structure factor $S(q)$ from the Fourier transformation of $g(r)$. In the low-q region $S(q)$ was also computed directly from its definition using the ensembles generated in the MC simulation.

In this region, the numerical evaluation of the Fourier transformation of $g(r)$ becomes unreliable because of the sensitivity of $S(q)$ to the behavior of $g(r)$ in the large-r region. By contrast, the direct determination of $S(q)$ from the definition leads to satisfactory results for low q, even though it is carried out only at points given by the periodic boundary condition. Fowler[14] was the first to use the latter technique for $S(q)$ in the low-q region. Day *et al.*[13] used Fowler's method to obtain the low-q values of $S(q)$ for liquid

Li, Na and K. Sun *et al.*[3] also used the same technique to obtain the low-q values of $S(q)$ for liquid Rb.

There have been several attempts[15–17] to evaluate the resistivity ρ and thermoelectric power Q of liquid Cs using Ziman's theory. In general, these lead to considerable discrepancies between the calculated and experimental values of both ρ and Q. Of particular interest is the lack of agreement in both the sign and magnitude between the calculated and experimental value of Q for liquid Cs metal. For liquid Rb, Sun *et al.*,[3] using the same pseudopotential formalism described in the current work, obtained a theoretical value of Q in good agreement with experiment even though his value of ρ was a factor of two different from the experimental data. However, for liquid Na and K, Sun[4] obtained good agreement for both ρ and Q.

The discrepancies in the electronic transport properties for the simple liquid metals are usually considered to be due to the use of an inaccurate structure factor $S(q)$ and or form factor $w(q)$ in the Ziman formula. Most reported calculations have used the local pseudopotential for $w(q)$ and either experimental data or hard-sphere values for $S(q)$. Several authors[11,18,19] have stressed the importance of the nonlocality in pseudopotential calculations. In particular, Day *et al.*[13] have showed that the use of a local approximation results in a considerable change in the phonon spectra, compared to a nonlocal calculation, even for so simple a metal as Na. Furthermore, Shimoji[20] has claimed that no choice of packing fraction and radius of hard-sphere can yield good agreement between a theoretical and experimental structure factor, and that the use of a pair potential calculated from a first-principles pseudopotential should yield a more accurate $S(q)$. Ziman[21(a)] has also argued that the discrepancy between calculated and experimental values of ρ and Q found by Sündstrom[15] for Cs is probably due to the use of inaccurate experimental structure factor in the low-q region where it must be obtained by extrapolation.

It is important to note that in the present work we have obtained a fully nonlocal pseudopotential calculated from first-principles and have used this pseudopotential in a MC simulation for the static structure factor. These have then been used in the Ziman theory to calculate, "self-consistently", the electronic transport properties of liquid Cs. By "self-consistent" we mean the same pseudopotential has been used for the form factor and for the static structure factor which is determined in the MC simulation.

In Section II, we outline the first-principles nonlocal pseudopotential formalism. The MC method for obtaining $g(r)$ and $S(q)$ is described in Section III. In Section IV, we describe the calculations, using the Ziman theory, for the resistivity ρ, thermoelectric power Q, and thermoelectric parameter ξ. The results and conclusions are discussed in Section V.

II PSEUDOPOTENTIAL AND PAIR POTENTIAL

The effective ion–ion pair potential $U(r)$ is calculated from the following equations:

$$U(r) = \frac{(z^*e)^2}{r} + \frac{2\Omega_0}{(2\pi)^3} \int F(q) e^{i\mathbf{q}\cdot\mathbf{r}} d^3q, \tag{1}$$

where $F(q)$ is the energy-wavenumber characteristic, Ω_0 is the volume per ion, and z^* is the effective valence and is associated with the orthogonalization hole. The first term in Eq. (1) is the direct Coulombic interaction between ions, while the second term is the indirect electronic contribution due to the electron–ion interaction. The energy-wavenumber characteristic $F(q)$ is given by

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

where W is the nonlocal pseudopotential and the function $G(q)$[22] is introduced to account for the screening effect of the conduction electrons.

In the off-diagonal matrix element, W can be separated into two parts, the bare potential W^B and the screening potential W^{SC}:

$$\langle \mathbf{k}|W|\mathbf{k}+\mathbf{q}\rangle = \langle \mathbf{k}|W^B|\mathbf{k}+\mathbf{q}\rangle + \langle \mathbf{k}|W^{SC}|\mathbf{k}+\mathbf{q}\rangle. \tag{3}$$

The bare potential matrix element is also separable into the two contributions,

$$\langle \mathbf{k}|W^B|\mathbf{k}+\mathbf{q}\rangle = \langle \mathbf{k}|V^C|\mathbf{k}+\mathbf{q}\rangle + \langle \mathbf{k}|W^R|\mathbf{k}+\mathbf{q}\rangle, \tag{4}$$

where V^C is the crystal potential arising from the nucleus and the charge distributions of core and conduction electrons, and W^R is the repulsive potential term that results from the orthogonalization of the conduction-electron states to the core states.

The crystal potential V^C has the following five contributions: (i) the potential due to the ion core, (ii) the conduction-band-core exchange, (iii) the correlation between conduction and core electrons, (iv) the potential due to the single OPW states of the conduction electron density, and (v) the screening due to the multiple OPW expression for the conduction electron states. The repulsive term $\langle \mathbf{k}|W^R|\mathbf{k}+\mathbf{q}\rangle$ is given by

$$\begin{aligned}\langle \mathbf{k}|W^R|\mathbf{k}+\mathbf{q}\rangle &= \sum_{n,1} \left(\frac{\hbar^2k^2}{2m} + \langle \mathbf{k}|V^C|\mathbf{k}\rangle - E_{n1}\right) \langle \mathbf{k}|n1\rangle\langle n1|\mathbf{k}+\mathbf{q}\rangle \\ &\quad + \sum_{n,1} \left(\frac{\hbar^2k^2}{2m} + \langle \mathbf{k}|V^C|\mathbf{k}\rangle - E_{n1}\right) \\ &\quad \times \langle \mathbf{k}|n1\rangle\langle n1|\mathbf{k}\rangle \frac{\langle \mathbf{k}|P|\mathbf{k}+\mathbf{q}\rangle}{1 - \langle \mathbf{k}|P|\mathbf{k}\rangle},\end{aligned} \tag{5}$$

where E_{nl} and $|nl\rangle$ are the eigenvalues and eigenfunctions of the ion, respectively, and P is the projection operator, $P = \sum_{n,l} |nl\rangle\langle nl|$, onto the core states.

The explicit **k**-dependence of $\langle \mathbf{k} | W^R | \mathbf{k} + \mathbf{q} \rangle$ reflects the nonlocal property of the pseudopotential W. Taylor *et al.*[11] have stated that nonlocality in a pseudopotential will produce qualitative changes in the physical properties compared to that calculated with a local pseudopotential. Similar views have been previously expressed by Sun *et al.*,[6] Day *et al.*[13] and Bertoni *et al.*[18] They have argued that nonlocality is important even for simple metals. For this reason we have consistently used the fully nonlocal pseudopotential throughout the calculations for the alkali metals including Cs.

The screening potential matrix element is given by

$$\langle \mathbf{k} | W^C | \mathbf{k} + \mathbf{q} \rangle = \frac{\langle \mathbf{k} | V^C | \mathbf{k} + \mathbf{q} \rangle (1 - \varepsilon(q))}{\varepsilon(q)} + \frac{2e^2(1 - G(q))}{\pi^2 \varepsilon(q) q^2} \int \frac{\langle \mathbf{k} | W^R | \mathbf{k} + \mathbf{q} \rangle d^3k}{(\hbar^2/2m)(k^2 - |\mathbf{k} + \mathbf{q}|^2)}, \tag{6}$$

where $\varepsilon(q)$ is the dielectric response function for the interacting conduction electron gas. The first term in Eq. (6) is simply the screening of the crystal potential while the second is the screening of the repulsive potential which has to be considered for the nonlocal pseudopotential formalism.

For the interacting electron gas, $\varepsilon(q)$ is given by

$$\varepsilon(q) = 1 + [1 - G(q)][\varepsilon^H(q) - 1], \tag{7}$$

where $\varepsilon^H(q)$ is the free-electron or Hartree dielectric constant, and $G(q)$, which accounts for the exchange and correlation effects, is the function derived self-consistently by Singwi *et al.* (SSTL).[5] The SSTL screening function is used because it satisfies the compressibility sum rule and yields reasonable values of the pair correlation function $g(r)$ for small r.

To calculate $F(q)$, the first-principles nonlocal pseudopotential scheme requires as input only the lattice constant, atomic number and atomic mass, and the eigenenergies and eigenfunctions of the ion. For liquids, the "lattice constant" is defined as the mean separation between neighboring atoms. In the present work, the "lattice constant" is determined from the measured density of liquid Cs at the melting point, which is equal to 1.843 g/cm^3.[23] The core energies and wave functions of Cs$^+$ were calculated using the Herman–Skillman[24] atomic program for Hartree–Fock–Slater theory. Using Eq. (1), we have evaluated $U(r)$ of liquid Cs at the melting point. This is given in Figure 1.

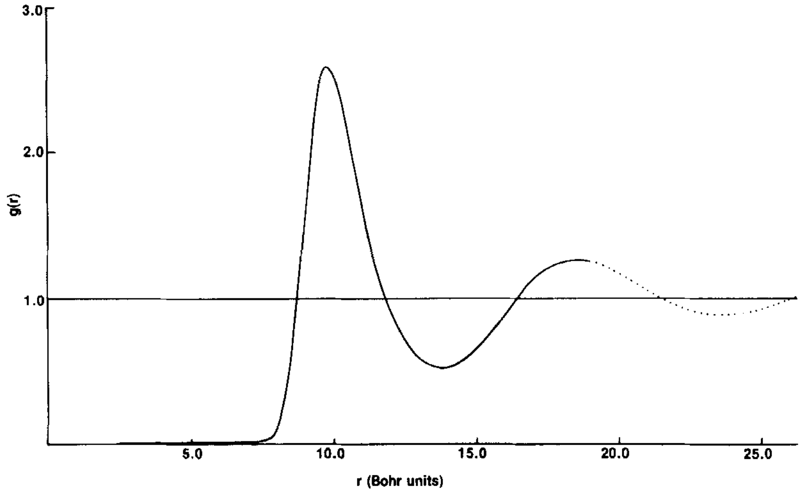

FIGURE 1 Pair potential $U(r)$ of liquid Cs at melting point (28.4°C) with mass density $d_{\mathrm{mp}} = 1.843$ g/cm^{3},[23] mean separation $a = 6.209$ Å, and effective valence $z^* = 1.224$.

III MONTE CARLO CALCULATION

The simulated system consists of 216 particles enclosed in a cubic box of edge length L of 55.89 atomic units (a.u.) with periodic boundary conditions. This system has the same mass density as liquid Cs at the melting point. We have generated about 300,000 configurations among which approximately half are accepted as members of the Markov chain. (Detailed discussions of the formal MC method have been given by Wood.[12])

The MC scheme first evaluates the cumulative function $G(r)$ which represents the total number of particles within a distance r from the origin. The pair correlation function $g(r)$ is then obtained from $G(r)$ using the relation

$$g(r) = \frac{1}{4\pi r^2 n_0}\frac{dG(r)}{dr}, \tag{8}$$

where n_0 is the average number density. The calculation for $g(r)$ is not started until the system has evolved to a stable liquid structure that occurs after approximately 200,000 configurations. For $r \geq 19$ a.u., i.e., in the region beyond the boundary of the simulated system, $g(r)$ is replaced by the asymptotic form[13,25]

$$g(r) \approx 1 + B\cos(2k_F r + \phi)/r^3, \tag{9}$$

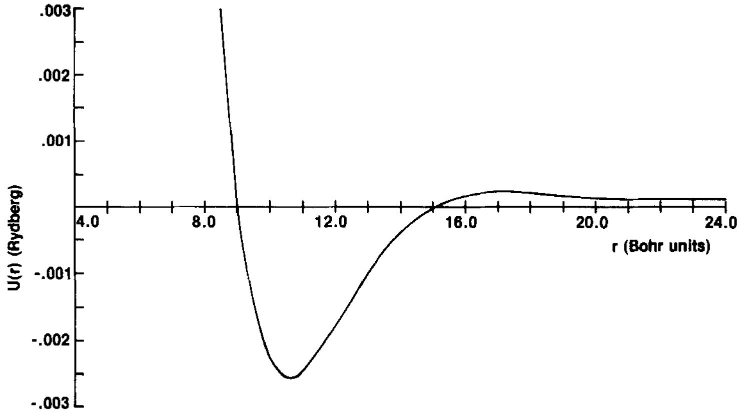

FIGURE 2 Pair correlation function $g(r)$ of liquid Cs at melting point. Monte Carlo simulation is used to find $g(r)$ for $r < 19$ a.u. For $r > 19$ a.u., the asymptotic form of $g(r)$ is used: $g(r) = 1 + B\cos(2k_F r + \phi)/r^3$, where $B = -1496$ (a.u.)^3 and $\phi = -9.25$.

where the constants B and ϕ are chosen so that there is a smooth transition between the two portions of the $g(r)$ curves given by Eqs (8) and (9). The resultant curve of $g(r)$ is shown in Figure 2.

Using the calculated values of $g(r)$, the structure factor $S(q)$ is evaluated from the Fourier transformation,

$$S(q) = 1 + n_0 \int e^{i\mathbf{q}\cdot\mathbf{r}}(g(r) - 1)d^3r. \qquad (10)$$

Even though Eq. (10) is an exact relation, it is difficult to calculate accurate values of $S(q)$ for low q. This is a consequence of the fact that the low-q values of $S(q)$ are sensitive to the large-r behavior of $g(r)$, which is approximated by Eq. (9). In addition, Eq. (10) cannot be numerically integrated over the whole infinite range of r. As in our previous works,[7,8,13] we have circumvented this difficulty by calculating $S(q)$ directly from the definition

$$S(q) = \frac{1}{N}\left\langle \left| \sum_i \exp(i\mathbf{q}\cdot\mathbf{r}_i) \right|^2 \right\rangle_{\mathrm{av}}, \qquad (11)$$

where N is the number of particles (i.e., 216), $\mathbf{r}_i$ are coordinates of ith particle, and $\langle\ \rangle_{\mathrm{av}}$ denotes an ensemble average in the configuration space. This procedure yields results which are consistent with the Fourier transformation calculation. Furthermore, in the low q-region, the use of Eq. (11) produces a monatomic curve whereas the Fourier transformation method produces unreasonable oscillations. Therefore we have used the low-q values of $S(q)$ obtained from Eq. (11) in the calculation of electronic transport properties.

Thermodynamically, the long wave-length limit of the structure factor $S(0)$ is given by

$$S(0) = n_0 k_B T \chi_T, \tag{12}$$

where χ_T is the isothermal compressibility. In this work the limiting value $S(0)$ is obtained by extrapolating the calculated curve of $S(q)$ to $q = 0$. With the righthand side of Eq. (12) evaluated using the experimental data for χ_T, we compare the extrapolated value of $S(0)$ to other theoretical and experimental values given in Table I. It is seen that the agreement is quite satisfactory.

TABLE I

Temperature T(°K), particle density $n_5(A^{-3})$, $S(0)$,[a] and $n_0 k_B T \chi_T$[b]

		T	n_0	S(0)	$n_0 k_B T \chi_T$
Theory	Present Work	302	0.00835	0.020	0.022[c] 0.024[d]
	Evans[32]	302	0.00833	0.027	
Exp.	Huijben[26]	303		0.026	0.022
	Faber[31]	303			0.028

[a] Obtained by extrapolating the $S(q)$ curve.
[b] Calculated from experimental values of χ_T.
[c] Used Huijben's data $\chi_T = 62 \times 10^{-12}$ cm²/dyne.
[d] Used Faber's data $\chi_T = 69 \times 10^{-12}$ cm²/dyne.

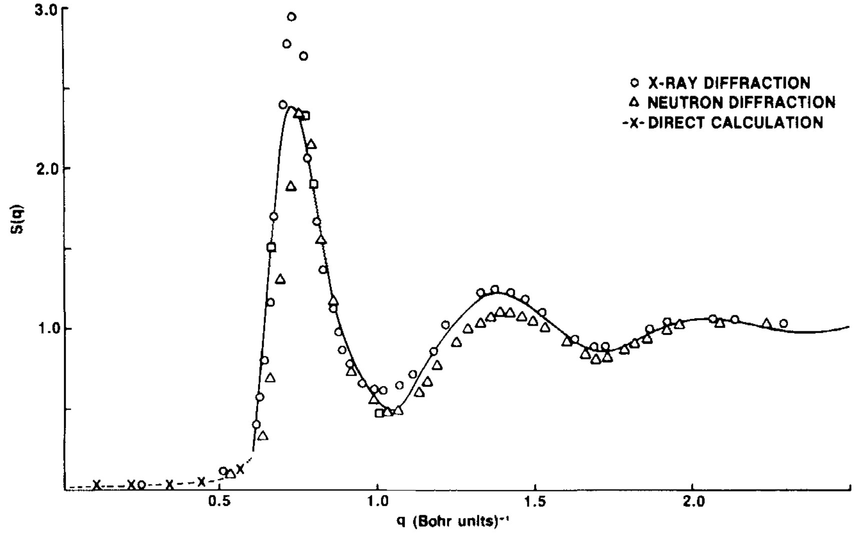

FIGURE 3 Structure factor $S(q)$ of liquid Cs at melting point. The experimental data are the X-ray diffraction measurements (○) of Huijben *et al.*[26] and neutron diffraction measurements (△) of Gingrich *et al.*[27] at 30°C. Theoretical values are obtained from the direct calculation of the definition (— x — and —□—) and Fourier transformation of $g(r)$ (full curve).

The stability of the MC simulated systems can be verified by first examining the curves of $g(r)$ and $S(q)$. Both curves should be smooth throughout the entire region. This is confirmed by the curves in Figures 2 and 3. In addition the thermodynamic relation, Eq. (12), should be satisfied if the simulated system is equivalent to, or closely approximates, the real system. We further verified the stability of the simulated liquid state by examining the electronic transport properties calculated as a function of increasing number of configurations in the statistical ensemble.

IV ELECTRICAL TRANSPORT PROPERTIES

The Ziman free electron theory of liquid metals leads to the following expressions for the electrical resistivity ρ, thermoelectric power Q, and thermoelectric parameter ξ:

$$\rho = \frac{3\pi m^*}{2\hbar e^2 E_F n_0} \langle S|w|^2\rangle \tag{13}$$

$$Q = -\frac{\pi^2 k_B^2 T}{3|e|E_F}\,\xi, \tag{14}$$

$$\xi = -\left[\frac{d(\ln \rho(E))}{d(\ln E)}\right]_{E_F}, \tag{15}$$

and

$$\langle S|w|^2\rangle = \int_0^1 S(q)|w(q, k_F)|^2 4(q/2k_F)^3 d(q/2k_F), \tag{16}$$

where $w(q, k_F)$ is the screened pseudopotential form factor $\langle \mathbf{k}|w|\mathbf{k} + \mathbf{q}\rangle_{E_F}$, m^* is the effective mass, and k_F and E_F are the Fermi wavevector and Fermi energy, respectively. Equation (15) can be written in the form

$$\xi = 3 - \alpha - \beta, \tag{17}$$

where

$$\alpha = \frac{2S(2k_F)|w(2k_F)|^2}{\langle S|w|^2\rangle}, \tag{18}$$

and

$$\beta = \frac{\left\langle S\left[\frac{d|w|^2}{d \ln E}\right]_{E_F}\right\rangle}{\langle S|w|^2\rangle}. \tag{19}$$

TABLE II

Electrical resistivity $\rho(\mu\Omega\ \mathrm{cm})$, thermoelectric power $Q(\mu V/°\mathrm{K})$ and thermoelectric parameter ξ.

		T(°K)	ρ	Q	ξ
Theory	Present Work	302	18.2	5.51	−1.12
	Sundstrom[15]	303	12.7	−5.9	+1.1
	William[16]		9.1[a]		
			20.4[b]		
	Rao[17]		18.9[c]		
			37[d]		
Exp.		302	36[34]		
	Kendal[38]	302		6.5	−1.31

[a] Used Heine–Abarenkov pseudopotential.

[b] Used the Optimized model potential.

[c] Used adjustable parameters associated with local pseudopotential calculations of the phonon spectra.

[d] Used adjustable parameters chosen arbitrarily.

The term β is the contribution from the k-dependence of the form factor evaluated at the Fermi energy and is usually neglected in the calculation of ξ. For the alkali metals Sündstrom[15] has used the approximation of $3 - \alpha$ to calculate ξ. He found fair agreement with the experimental values except for Cs. Ziman[21(a)] has pointed out that the discrepancy for Cs is probably due to the use of the inaccurate experimental structure factor. In the present work we also evaluate the thermoelectric parameter ξ, neglecting β. The results of the present calculations are given in Table II. These are discussed in the next section.

V RESULTS AND DISCUSSIONS

As shown in Figure 3, the theoretical curve for $S(q)$ is generally in good agreement with the X-ray experimental data of Huijben *et al.*[26] except for the height of the main peak, $S_{\max}(q)$. The computed value of $S_{\max}(q)$ is about 0.5 lower than the X-ray experimental value. However, the main peak occurs at $q = 0.747\ (\mathrm{a.u.})^{-1}$, which is the same as obtained from the X-ray data. In Figure 3, we also show, for purposes of comparison, the curve of $S(q)$ obtained from the neutron scattering data of Gingrich *et al.*[27] In particular, Huijben has stressed the significant difference between the X-ray and neutron scattering determinations of the $S(q)$ curve.

It has been suggested by Egelstaff[28] that the difference in the peak heights between the two experimental values of $S(q)$ is attributed to the different correlation effects of electrons and ions. From this point of view, the present results are expected to be more consistent with the X-ray rather than the neutron data because the present calculations of $S(q)$ are done with the pair potential that includes the electron correlation effects. For $S(q)$ calculated by Day *et al.*[13] for Na and K and by Sun *et al.*[2] for Rb, the peak heights are also somewhat smaller than the X-ray experimental values. This, combined with the present results for Cs, suggests a systematic discrepancy in the height of the main peak of $S(q)$ between the X-ray measurements and theoretical calculations. A possible reason for this is the overestimation of the effect of the depletion of core electron density, i.e., orthogonalization hole,[2,3] in the pseudopotential formalism. This implies a reduction in the correlation effects of the core electrons, which, in turn, contributes to the broadening of the peak and the lowering of the whole curve. A more rigorous theory, including a self-consistent treatment of the core electron density, is probably necessary to resolve this discrepancy.

According to the X-ray experimental data of Huijben *et al.*,[26] Zei[29] and Greenfield,[30] the main peak of $S(q)$ occurs at about $q \approx 2.24k_F$ for all alkali metals. This is also obtained from the theoretical $S(q)$ in the present work for Cs. Similar results can be obtained in the calculations of Day *et al.* and Sun *et al.* for the $S(q)$ curves of Na, K and Rb. We note that the empirical relation, $q_{\max} \approx 2.4k_F z^{-1/3}$, is reasonably satisfied for all the simple and non-transition polyvalent metals, where $q_{\max}$ is the position of the main peak and z is the valence of the ion. The observation that $q_{\max}$ can be given empirically in terms of k_F is significant since no prediction of $q_{\max}$ is theoretically known for liquid metals. In addition, it suggests that the present calculation of $S(q)$ is probably more consistent with X-ray rather than neutron scattering data, in agreement with our previous arguments.

The limiting value $S(0) = 0.020$ is obtained by extrapolating $S(q)$ to the point $q = 0$ (see Table I). For low q, the points $(q, S(q))$ are evaluated using Eq. (11). The values of q are determined from the periodic boundary conditions in the Monte Carlo simulation. The first five points are (0.1124, 0.02133), (0.2248, 0.03458), (0.3372, 0.04064), (0.4496, 0.07481) and (0.5620, 0.14459). It is seen from Table I that the thermodynamic relation expressed in Eq. (12) is better satisfied by Huijben's value of χ_T, using our value of $S(0)$, rather than Faber's.[31] Evans[32] obtained $S(0)$ analytically for all alkali metals, using Aschcroft's empty-core local pseudopotential,

$$-(4\pi z e^2/q^2)\cos(qR_c),$$

with the core radius R_c as an adjustable parameter.

As shown in Table II, the present value of $Q = 5.51\ \mu\text{V}/^\circ\text{K}$ is in good agreement with experiment. It is important to note that the present value of Q is positive, which agrees with the experimental result; this is in contrast with other theoretical predictions.[15] However, the resistivity $\rho = 18.2\ \mu\Omega\,\text{cm}$

is in disagreement with the experimental value $\rho = 36\ \mu\Omega$ cm. It is interesting to note that the calculated resistivity is rather close to the experimental value of $\rho = 21.7\ \mu\Omega$ cm for solid Cs metal. Sun *et al.* also obtained, for liquid Rb, similar results as those obtained here for liquid Cs. However, he found good agreement between the calculated and experimental values of ρ and Q for both Na and K.

Since the d-band states can be a factor in the electronic transport properties for the heavier alkali metals, Moriarty[33] has developed the zero-order pseudoatom model to consider s–d hybridization. He has found that the agreement of the resistivity with experiment is improved for the heavy alkali and alkali-earth metals although the agreement is less satisfactory for the group IIIb metals when the hybridization is included. It is also found that hybridization can result in poorer agreement for some properties, e.g., the pseudopotential form factor. In addition, the phonon dispersion relations of Rb using the pseudoatom technique with the s–d hybridization do not yield better agreement with experiment than obtained with the pseudopotential calculation of Sun *et al.*[2] This is illustrated in Table III.

It is known[21,31] that Ziman's NFE formula is particularly sensitive to small changes in the pseudopotential near $2k_F$. The low-q values of $S(q)$ is also crucial for the electronic transport properties of liquid metals. Faber[31] has discussed the different circumstances under which Ziman's formula of resistivity is not able to yield satisfactory results even though both the pseudopotential and structure factor are considered correct. For one of those cases, he considers the possibility that the density of states $n(E)$ for liquid metals will be different from that for free electrons. Experiments such

TABLE III

Phonon frequencies of Rb and Cs at several symmetry points (in 10^{12} Hz).

		$L[100]$	$L[110]$	$T_1[110]$	$T_2[110]$
Rb	Sun *et al.*[a]	1.47	1.64	0.35	0.97
	Moriarty[b]	1.37	1.60	0.27	0.92
	Moriarty[c]	1.40	1.63	0.27	0.93
	Exp.[d]	1.39	1.50	0.34	0.96
Cs	Chung *et al.*[9]	1.06	1.20	0.23	0.72
	Taylor *et al.*[11]	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

[a] Used the same pseudopotential formalism explained in the present work or in the phonon calculation of Chung *et al.*[9] for Cs.

[b] Pseudoatom model calculation without s–d hybridization.

[c] Pseudoatom model calculation with s–d hybridization.

[d] J. R. D. Copley and B. N. Brockhouse, *Can. J. Phys.* **51**, 657 (1973).

as Knight shift, optical absorption and Hall effect on free-electron-like liquid metals have not always shown the features of the free electron density of states,[21,31,34] e.g., $n(E)\alpha E^{1/2}$. A possible explanation of these ambiguous results can be suggested by treating a liquid metal in terms of a disordered system theory.[35,36] The topological disorder, i.e., random potential, in liquid metals can lead to the loss of the long-range order or fluctuations in the particle density. This mechanism can produce changes in the shape of $n(E)$ and, at a critical value of the density fluctuation (i.e., randomness), can cause itinerant (i.e., Bloch) electron states to localize. A change in the magnitude of $n(E)$ is thus always probable for liquid metals. However, small variations in $n(E)$ are known to produce little effect on the electronic transport properties.[21] Mott[35(b)] has argued that the mean free path would become comparable with the electron wavelength if the ratio $n(E)/n_{\mathrm{free}}(E)$ is smaller than one half. He has further argued that even the localization of a Bloch state must occur for small values of the density ratio. For that situation, the basic assumption of a NFE approximation for Ziman's theory will be meaningless and a different approach, such as the T-matrix formalism, is required.

In a recent paper, Ito[37] has presented an analysis, based on the Roth[38] theory, which he claims leads to several corrections of Ziman's formula; in particular, he asserts that the free electron mass in the formula is to be replaced by an effective mass defined from the relation between the group velocity and the "liquid dispersion", where the latter is determined by the singularity of the one-particle Green function. However, he did not present any actual calculations from which to estimate the significance of his effective mass corrections.

In summary, the present work for Cs as well as that of Sun *et al.* for Rb seems to indicate the necessity of some modifications or corrections to Ziman's formula when applied to the heavy alkali metals. To explain the electronic transport properties in these metals, it may be necessary to use an effective medium theory such as that developed by Roth for the electronic structure of liquid metals. The inclusion of s–d hybridization, as suggested by Moriarty, in a more general pseudopotential formalism may also contribute to an accurate theory of the electronic transport properties for the heavier liquid alkali metals.

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