

Transport of electrons in compressed Li, Na, and K: Thermoelectric powers, resistivities, and Hall coefficients

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The diffusion-thermoelectric power coefficients, resistivities, and Hall coefficients of Li, Na, and K are computed for high temperatures as functions of pressure using a relaxation-time approximation solution to the Boltzmann equation. The electron-phonon interaction is treated in a rigid-ion model, the electrons are assumed free, and the ion structure factor is constructed from pressure-dependent elastic-constant data. Account is taken of anisotropic scattering, nonlocal-pseudopotential effects, and the "kinetic-anisotropy" effect, all of which are important. The agreement between theory and experiment is generally very good, the small discrepancies between theoretical and experimental values of the transport coefficients being directly ascribable to uncertainties in the pseudopotentials and structure factors employed. Surprisingly, the thermoelectric powers and their pressure dependences are less sensitive to details of the pseudopotentials than the resistivities. These calculations suggest that large thermoelectric-power coefficients are associated with anisotropic (as well as energy-dependent) scattering, and with pseudopotentials $V(q)$ such that the product of $|V(q)|$ and $d|V|/dq$ is large for q near $2k_F$.

I. INTRODUCTION

Although Bardeen's successful computation¹ of the resistivity of sodium in 1937 inaugurated the microscopic theory of electronic transport in metals, thermoelectric transport properties remain somewhat puzzling even today. Both simple theory and intuition suggest that the thermopower, $S \equiv \bar{E}/\bar{V}T$, should have the same sign as the principal charge carrier. Experimentally²⁻⁴ we find, however, positive thermopowers for Li and the noble metals Cu, Ag, and Au. Studies of the effects of Fermi-surface geometry, notably by Ziman,⁵ have presented a plausible explanation of the positive thermopowers of the noble metals, whereas Robinson's⁶ demonstration that lithium's positive thermopower could be attributed to the energy dependence of the electron's mean free path provided an explanation of the last major thermoelectric anomaly.

Although the essential macroscopic physics relating the resistivities, Hall coefficients, and thermopowers to mean free paths is understood, no convincing, detailed, and quantitatively successful microscopic theory of mean free paths and their energy dependences has been reported.

In this paper, we report calculations of the high-temperature phonon-limited mean free paths and computations of the electronic-transport coefficients of Li, Na, and K as functions of pressure. We show that the differences between theoretical and experimental values are small and directly ascribable to uncertainties in the parameters of the model (e.g., pseudopotentials, force constants) at all pressures. We demonstrate that "kinetic-anisotropy" effects⁷ and nonlocal electron-ion scattering⁸ are important, and nec-

essarily play dominant roles in any quantitative theory of electronic transport. We find that reliable values of the thermoelectric powers of Li, Na, and K are easily calculated and less sensitive than the resistivities to the choice of pseudopotential.

Section II discusses the model, Sec. III the computations, and Sec. IV our results. Comments and conclusions are made in Sec. V.

II. MODEL

A. Elements

The computations of this paper are based upon a relaxation-time-approximation solution⁹ to the Boltzmann equation for the mean free path $l(\vec{k})$,

$$\frac{1}{l(\vec{k})} = \frac{\Omega}{8\pi^2} \frac{m^{*2}}{\hbar^4 k^4} \int d^3q q |V(q, \vec{k}, E(\vec{k}))|^2 \times S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right). \quad (1)$$

Here the electrons are assumed to be free with the dispersion relation $E(\vec{k}) = \hbar^2 k^2 / 2m^*$ and the electron-ion interaction is treated in a rigid-ion model. V is the screened single-ion pseudopotential, Ω is the cell volume, and $S(\vec{q})$ is a static approximation to the dynamic structure factor or ion density-fluctuation correlation function:

$$S(\vec{q}, \omega) \approx S(\vec{q}) \delta(\omega), \quad (2a)$$

$$S(\vec{q}, \omega) = \frac{1}{2\pi N} \int dt e^{-i\omega t} \langle \rho(-\vec{q}, t) \rho(\vec{q}, 0) \rangle_T \quad (2b)$$

in the standard notation.¹⁰ [The prime on $S'(\vec{q})$ signifies the omission of the Bragg reflections associated with the static lattice.]

The macroscopic transport coefficients are given in terms of the mean free paths.¹¹ For the electrical conductivity σ , we have

$$\sigma = \frac{e^2}{12\pi^3\hbar} \int l(\vec{k}) dS(E_F), \quad (3)$$

where $dS(E)$ is an element of area on a surface of constant energy E in the Brillouin zone, e is the charge of the electron ($e = -|e|$), and $E_F = \hbar^2 k_F^2 / 2m^*$ denotes the Fermi energy. For the Hall coefficient R_H , and the thermopower, we have

$$R_H = \frac{e^3}{12\pi^3\hbar cm^* \sigma^2} \int \frac{l^2(\vec{k})}{|\vec{v}(\vec{k})|} dS(E_F), \quad (4)$$

$$S = \frac{\pi^2 k_B^2 T}{3e} \frac{\partial}{\partial E} \left(\ln \int l(\vec{k}) dS \right) \Big|_{E=E_F}; \quad (5)$$

c denotes the speed of light in vacuum, k_B is Boltzmann's constant, and T is the temperature.

To simplify our computations, we follow earlier work⁹ and replace the integrals over the Fermi surface by sums over wave vectors limited to the principal symmetry directions ([100], [110], and [111]),

$$\sigma = \frac{e^2 n}{\hbar k} \left(\sum_{\hat{k}} l(\vec{k}) \right) / \left(\sum_{\hat{k}} 1 \right) \Big|_{k=k_F}, \quad (6)$$

$$R_H = 1/n^* e c, \quad (7a)$$

$$\frac{n^*}{n} = \left[\left(\sum_{\hat{k}} l(\vec{k}) \right)^2 / \left(\sum_{\hat{k}} l^2(\vec{k}) \right) \left(\sum_{\hat{k}} 1 \right) \right] \Big|_{k=k_F}, \quad (7b)$$

$$S = \frac{\pi^2 k_B^2 T}{3e E(\vec{k})} \left(\sum_{\hat{k}} l(\vec{k}) \xi(\hat{k}) / \sum_{\hat{k}} l(\vec{k}) \right) \Big|_{k=k_F}, \quad (8)$$

$$\xi(\hat{k}) = 1 + \frac{\partial \ln l(\vec{k})}{\partial \ln E(\vec{k})} \Big|_{k=k_F}. \quad (9)$$

Here n is the density of conduction electrons and n^*/n is a number of order unity which accounts for the anisotropy of the scattering.

The transport coefficients are evaluated by (i) specifying a structure factor $S'(\vec{q})$ and a pseudopotential $V(q, \vec{k}, E(\vec{k}))$; (ii) computing a mean free path $l(\vec{k})$; and (iii) evaluating the relevant averages [Eqs. (6-9)] of $l(\vec{k})$.

B. Structure factor $S'(\vec{q})$

The structure factor $S'(\vec{q})$ is most easily determined from neutron scattering data. Although such data exist for zero pressure for Li,¹² Na,¹³ and K,¹⁴ pressure-dependent data are not yet available. Therefore, we construct $S'(\vec{q})$ by converting pressure-dependent elastic constant

data¹⁵⁻¹⁷ into pressure-dependent force constants, by assuming a three-force-constant Born-von K arm an model of the lattice dynamics.

This three-force-constant model has been discussed for the case of zero pressure⁹ and leads to typical errors in $S'(\vec{q})$ of 10%. Uncertainties in the values of the elastic constants, especially at high pressures, are unlikely to cause additional uncertainties of more than 5% in the structure factor. The structure factor is

$$S'(\vec{q}) = (k_B T / M) \vec{q} \cdot \underline{D}^{-1}(\vec{q}) \cdot \vec{q}, \quad (10)$$

where M is the ionic mass and $\underline{D}(\vec{q})$ is the dynamical matrix¹⁸ obtained by appropriately Fourier transforming the force-constant matrix. Terms of higher order in powers of Θ_D/T have been omitted, where Θ_D is the Debye temperature. (The data reveal room-temperature thermopowers and resistivities linear in T .)^{19,20}

The primary advantages of this model are (i) it permits a detailed assessment of the anisotropy of the scattering, since the full-point group symmetry is automatically incorporated into the structure factor $S'(\vec{q})$; (ii) umklapp scattering processes⁹ are automatically handled by virtue of the space-group periodicity of $S'(\vec{q})$; and (iii) the pressure dependence of $S'(\vec{q})$ is determined by experimental data.

The derivative of the structure factor is

$$\begin{aligned} \frac{\partial S'}{\partial q}(\vec{q}) &= \vec{q} \cdot \vec{\nabla}_{\vec{q}} S'(\vec{q}) = \frac{k_B T}{M} \vec{q} \cdot \nabla_{\vec{q}} \vec{q} \cdot \underline{D}^{-1} \cdot \vec{q} \\ &= \frac{2S'(\vec{q})}{q} + \frac{k_B T}{M} \vec{q} \cdot (\vec{q} \cdot \vec{\nabla}_{\vec{q}} \underline{D}^{-1}) \cdot \vec{q}. \end{aligned} \quad (11)$$

C. Pseudopotentials

The pseudopotentials are taken to be either Lee's augmented-plane-wave pseudopotential²¹ or the Heine-Abarenkov pseudopotential^{22,23} (hereafter referred to as the APW and HA pseudopotentials, respectively). The differences are typically (10-20)% (see Fig. 1).

D. New features of the present calculations

Our computations include both nonlocal pseudopotential effects and "kinetic-anisotropy" effects,⁷ which influence the thermoelectric power, but not the conductivity or Hall coefficient.

In obtaining the partial thermopower coefficient [Eq. (9)]

$$\xi(\hat{k}) = 1 - \left(\frac{d \ln l^{-1}(\vec{k})}{d \ln E(\vec{k})} \right) \Big|_{k=k_F},$$

there are four contributions to the derivative of $l^{-1}(\vec{k})$ [see Eq. (1)]: (i) from the explicit dependence of the k^{-4} prefactor; (ii) from the integra-

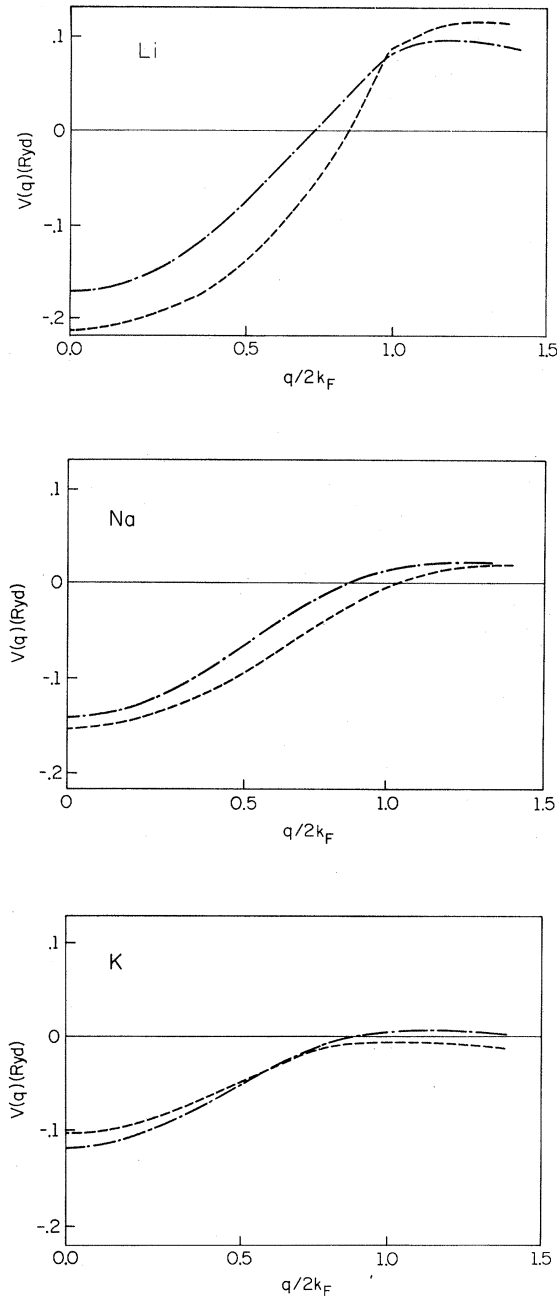


FIG. 1. Pseudopotential $V(q, \vec{k}, E(\vec{k}))$ vs wave-vector transfer q for Li, Na, and K (evaluated at the Fermi surface for zero pressure). The dashed and alternating dash-dot lines refer to pseudopotentials given by Lee (Ref. 21) and Animalu and V. Heine (Ref. 23), respectively.

tion limit $2k$ [which comes from the δ function in Eq. (1)]; (iii) from the (nonlocal) pseudopotential $V(q, \vec{k}, E(\vec{k}))$; and (iv) from the anisotropy of the structure factor. The first two were accounted for by Robinson and Dow⁹; the third is the "non-local-pseudopotential effect" discussed by Borto-

lani and Calandra⁸; and the fourth is the "kinetic-anisotropy" effect.⁷ The simple theory had hoped to omit both non-local-pseudopotential and kinetic-anisotropy effects while sacrificing only the ability to quantitatively compute the anisotropy of the partial thermopowers $\xi(\vec{k})$. However, nonlocal effects are significant in all the alkalis⁸ and demonstrably so in K.²⁴ Furthermore, the kinetic-anisotropy effect is especially large in Li or any metal for which the scattering is both anisotropic and a strong function of the electron's kinetic (Fermi) energy; it gives rise to a dramatically different form for the dependence of ξ on the pseudopotential.

Directly differentiating the inverse mean free path, we find

$$\xi(\hat{k}) = 1 + 2 - \frac{1}{2} r(\hat{k}) - u(\hat{k}), \quad (12)$$

where Bortolani's and Calandra's⁸ non-local-pseudopotential contribution is

$$\begin{aligned} r(\hat{k}) = & k \int d^3q q \frac{\partial}{\partial k} |V(q, \vec{k}, E(\vec{k}))|^2 S'(\vec{q}) \\ & \times \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) / \int d^3q q |V(q, \vec{k}, E(\vec{k}))|^2 \\ & \times S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) \Big|_{k=k_F}, \end{aligned} \quad (13)$$

and we have

$$\begin{aligned} u(\hat{k}) = & \frac{k}{2} \int d^3q q |V(q, \vec{k}, E(\vec{k}))|^2 S'(\vec{q}) \\ & \times \frac{\partial}{\partial k} \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) / \int d^3q q \\ & \times |V(q, \vec{k}, E(\vec{k}))|^2 S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) \Big|_{k=k_F}. \end{aligned} \quad (14)$$

There are two simple methods for differentiating the δ function in Eq. (14); the first uses the identity

$$\frac{\partial}{\partial k} \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) = \frac{-q}{2k^2} \frac{\partial}{\partial (\hat{q} \cdot \hat{k})} \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) \quad (15)$$

and results in

$$u(\hat{k}) = 2q(\hat{k}) + a(\hat{k}), \quad (16)$$

where $q(\hat{k})$ is well known^{8,9}

$$\begin{aligned} q(\hat{k}) = & 4k^4 |V(2k, \vec{k}, E(\vec{k}))|^2 S'(-2\vec{k}) / \\ & \int d^3q q |V(q, \vec{k}, E(\vec{k}))|^2 S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) \Big|_{k=k_F}, \end{aligned} \quad (17)$$

and $a(\hat{k})$ is the "kinetic anisotropy" neglected in most treatments

$$\begin{aligned}
a(\hat{k}) &= \frac{1}{4k} \int d^3q q^2 |V(q, \vec{k}, E(\vec{k}))|^2 \\
&\times \frac{\partial S'(\vec{q})}{\partial (\hat{q} \cdot \hat{k})} \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) / \int d^3q \\
&\times q |V(q, \vec{k}, E(\vec{k}))|^2 S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) \Big|_{k=k_F} .
\end{aligned} \tag{18}$$

Observe that, if the structure factor $S'(\vec{q})$ is isotropic, the term $a(\hat{k})$ vanishes, and the expressions of Robinson and Dow, as modified by Bortolani and Calandra, are recovered

$$\xi(\hat{k}) = 3 - 2q(\hat{k}) - \frac{1}{2}r(\hat{k}). \tag{19}$$

The basis of the kinetic anisotropy can be seen by considering the value of $S'(\vec{q})$ on a sphere of constant radius (constant q) (see Fig. 2). The product of $S'(\vec{q})$ and the energy-conserving δ function $\delta(\hat{q} \cdot \hat{k} + q/2k)$ is nonzero only on a circle of that sphere, the angle subtended by the circle being $\theta = \cos^{-1} \hat{q} \cdot \hat{k}$, a function of $|\vec{k}|$. Thus, the integral of $S'(\vec{q})$ over the energy conserving circle

$$\int_0^{2\pi} d\phi \int_{-1}^1 d(\hat{q} \cdot \hat{k}) S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right), \tag{20}$$

is also a function of $|\vec{k}|$, its detailed variation with $|\vec{k}|$ depending upon the weighting of the integrand by the anisotropy of $S'(\vec{q})$.

A convenient way to account for the kinetic-anisotropy effect is to use the identity

$$\frac{\partial}{\partial k} \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) = -\frac{q}{k} \frac{\partial}{\partial q} \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right), \tag{21}$$

which gives

$$\xi(\hat{k}) = -\frac{1}{2}r(\hat{k}) + d(\hat{k}) + s(\hat{k}), \tag{22}$$

where we have the derivative term

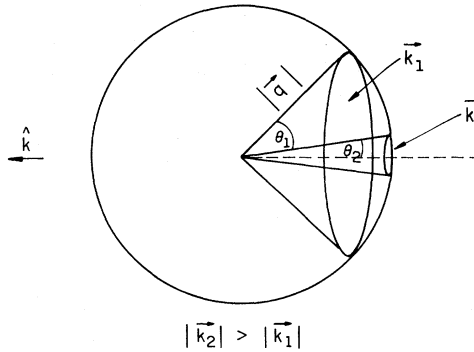


FIG. 2. Illustrating the kinetic anisotropy effect. For two different values of \vec{k} (\vec{k}_1 and \vec{k}_2) directed to the left, the corresponding energy conserving circles in the mean-free-path integrals equation (1) (indicated by the arrows) are different.

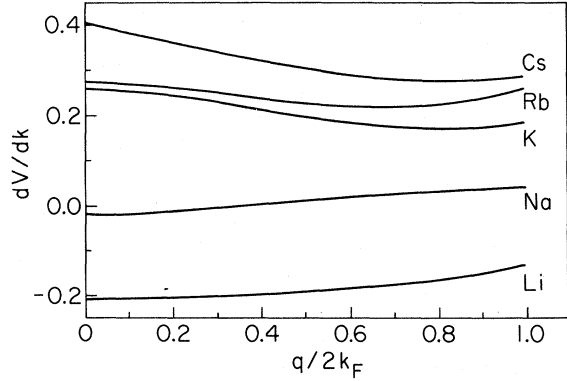


FIG. 3. Derivatives of the pseudopotentials of Ref. 23 with respect to the magnitude of the incident wave vector k (evaluated on the Fermi surface) vs wave-vector transfer q , as given by Ref. 8. The units of the derivative are Rydberg-Bohr-radius.

$$\begin{aligned}
d(\hat{k}) &= -\frac{1}{2} \int d^3q q^2 \frac{\partial}{\partial q} |V(q, \vec{k}, E(\vec{k}))|^2 \\
&\times S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) / \int d^3q q |V(q, \vec{k}, E(\vec{k}))|^2 \\
&\times S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) \Big|_{k=k_F} .
\end{aligned} \tag{23}$$

and

$$\begin{aligned}
s(\hat{k}) &= -\frac{1}{4\pi} \frac{k_B T}{M} \int d^3q q |V(q, \vec{k}, E(\vec{k}))|^2 \\
&\times \vec{q} \cdot (\vec{q} \cdot \nabla_q D^{-1}) \cdot \vec{q} \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) / \\
&\int d^3q q |V(q, \vec{k}, E(\vec{k}))|^2 S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) \Big|_{k=k_F} .
\end{aligned} \tag{24}$$

This form, Eq. (22), is more convenient for com-

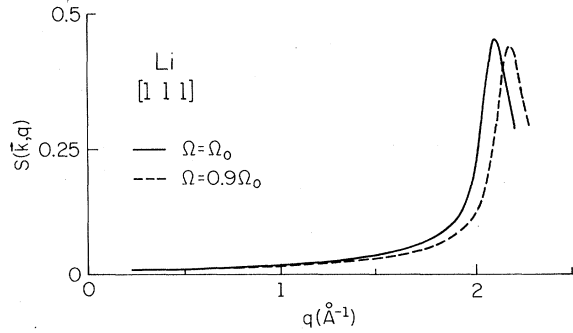


FIG. 4. Integral over angles of the structure factor, $S(k, q) = (1/2\pi) \int S'(\vec{q}) \delta(\hat{q} \cdot \hat{k} + q/2k) d\Omega_q$ vs wave-vector transfer q for k_F in the [111] direction for Li. The solid and dashed lines correspond to values for the normal cell volume and compression to 90% of the normal cell volume, respectively.

TABLE I. Values of the nonlocal contribution to $\xi(\hat{k})$ taken from Bortolani and Calandra (Ref. 8) with the value for K corrected for nonlocal-pseudopotential effects, as indicated by Lee and Falicov (Ref. 24).

$\frac{1}{2}r(\hat{k})$	Li	Na	K
[100]	-1.1	0.0	-4.2
[110]	-1.3	0.2	-1.2
[111]	-1.3	0.2	-0.6

putations, having an integrand free of singular behavior. The important features of Eq. (23) are its dependence on $\partial |V|^2/\partial q$ (which is different from the dependence found by Robinson and Dow), and the fact that it does not depend explicitly on the pseudopotential evaluated at $q=2k_F$. Of course, for small phonon anisotropies, $S'(\vec{q}) \approx S'(|\vec{q}|)$, the two theories coincide.

III. COMPUTATIONS

A. Pseudopotentials

In computing the transport properties of Li, Na, and K, we use the APW semiempirical-pseudopotential form factors²¹ and the HA screened pseudopotentials.²³ The pressure-dependence of the pseudopotentials was accounted for by simply altering a normalization factor of unit cell volume Ω . (The pseudopotential is inversely proportional to the volume Ω .) Efforts to account for pressure-dependence of the dielectric screening (by altering

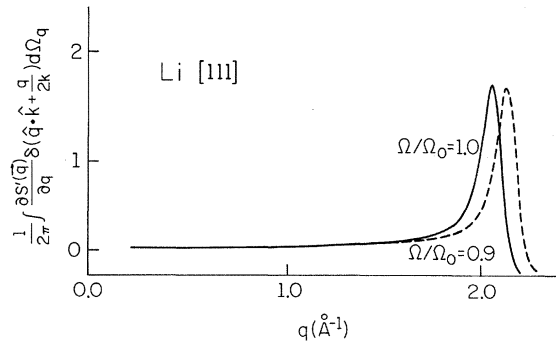


FIG. 5. Integrated derivative of the structure factor $(1/2\pi) \int [\partial S'(\vec{q})/\partial q] \times \delta(\hat{q} \cdot \hat{k} + q/2k) d\Omega_q$ vs wave vector transfer q , evaluated for $\vec{k}=\vec{k}_F$ in the [111] direction for Li. The solid and dashed lines correspond to values for the normal cell volume and compression to 90% of the normal cell volume, respectively.

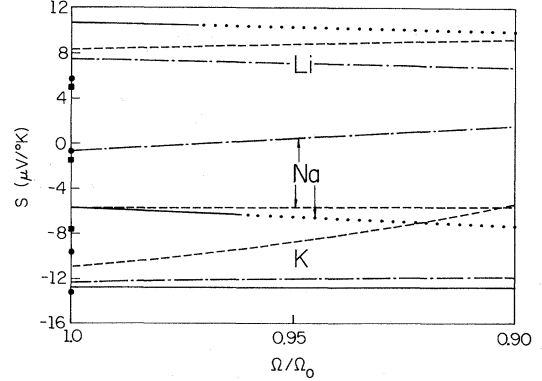


FIG. 6. Thermoelectric powers S (in $\mu\text{V}/^\circ\text{K}$) vs cell volume (in units of zero pressure cell volume) for Li, Na, and K. The solid and dotted lines refer to experiment and extrapolation of experiment, respectively. The dashed and alternating dash-dot lines refer to calculations using the APW and HA pseudopotentials, respectively. The solid squares and circles indicate zero pressure calculations of Refs. 9 and 8, respectively. Note that the lowest solid circle is for K, using three times the nonlocal correction given by Bortolani and Calandra, as is indicated in the text.

the Fermi energy) led to insignificant changes in the pseudopotentials. These pseudopotentials are given in Fig. 1.

The nonlocal contributions $(\partial V/\partial k)_{k=k_F}$ taken from work by Bortolani and Calandra⁸ are reproduced in Fig. 3. For potassium, de Haas-van Alphen measurements²⁴ reveal that Bortolani and Calandra underestimated $\partial V/\partial k$ by approximately a factor of 3; therefore we use the revised value in Table I, which produces good agreement with those measurements on K. The nonlocal effects change the thermopowers of Li, Na, and K by -1.7 , 0.3 , and $-5.5 \mu\text{V}/^\circ\text{K}$, respectively.

B. Structure factors

A typical structure factor (for Li, \hat{k} in the [111] direction) integrated over solid angles with the energy-conserving δ function is given in Fig. 4,

$$S(\vec{k}, q) = \frac{1}{2\pi} \int d\Omega_q S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) \Big|_{k=k_F}. \quad (25)$$

TABLE II. Ratio of thermopower S in $\mu\text{V}/^\circ\text{K}$ to reduced thermopower ξ at $T = 273.15^\circ\text{K}$. The ratio is linear in cell volume over the region given.

Ω/Ω_0	Li	Na	K
1.00	-1.420	-2.122	-3.174
0.90	-1.324	-1.978	-2.958

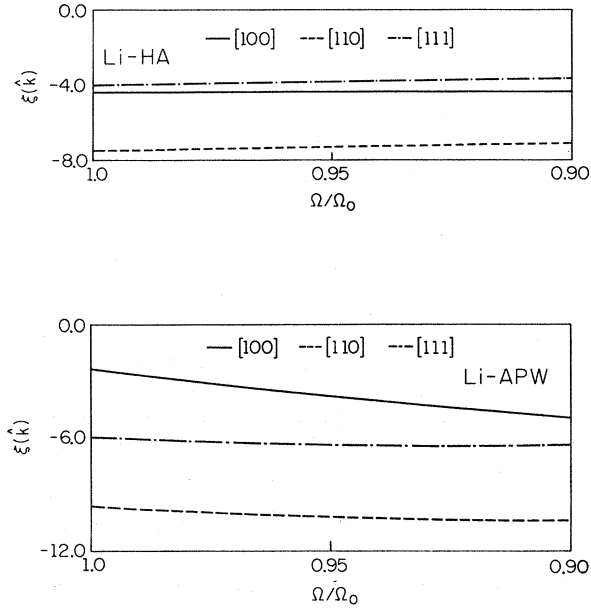


FIG. 7. Calculated partial thermoelectric powers $\xi(\hat{k})$ for the principal symmetry direction in Li as a function of cell volume Ω (in units of zero-pressure volume Ω_0). The solid, dashed, and dash-dot lines refer to the [100], [110], and [111] directions, respectively. The results labeled HA and APW were obtained using the pseudopotentials of Ref. 23 and Ref. 21, respectively.

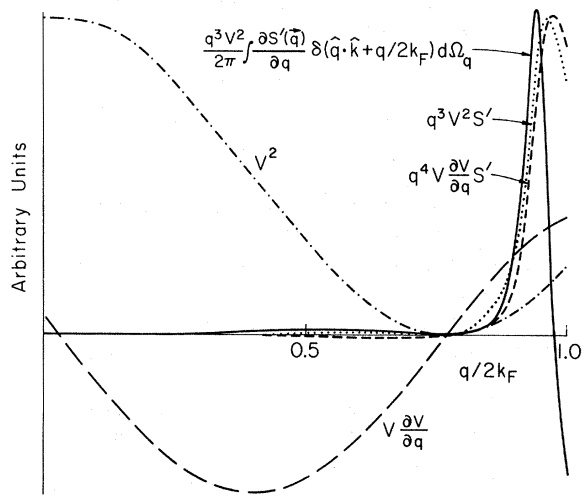


FIG. 8. Various quantities involved in calculating the partial thermopower coefficient versus wave vector transfer q (in units of twice the Fermi momentum k_F). Curves given are for Li in the [111] direction using the HA pseudopotential.

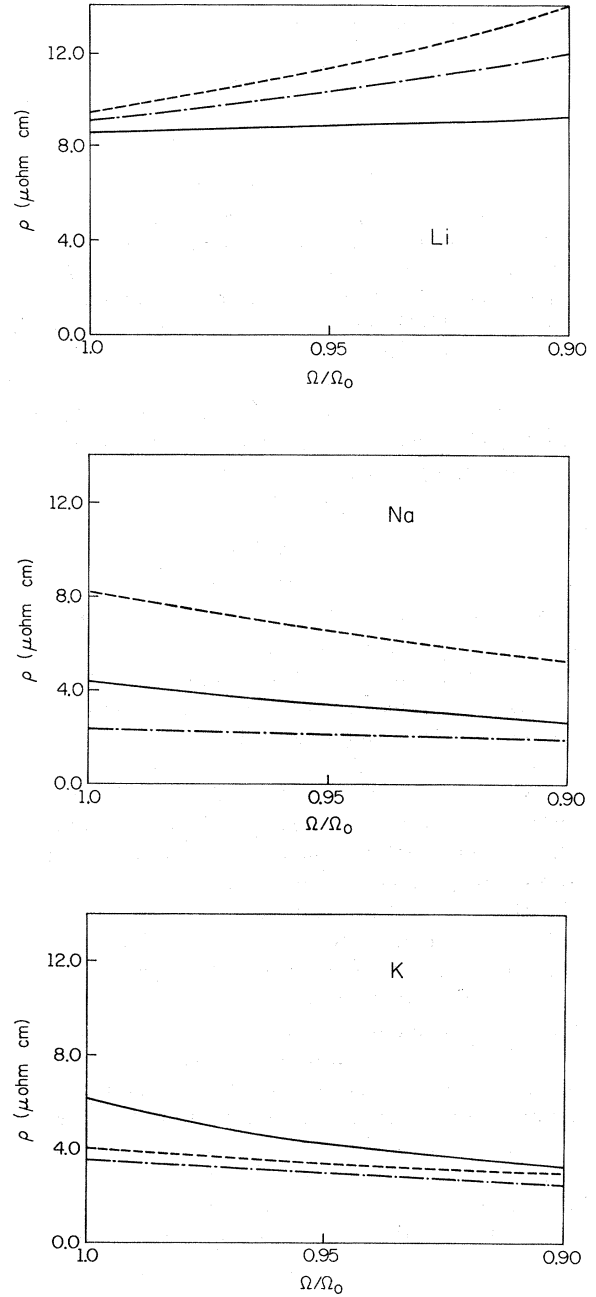


FIG. 9. Electrical resistivities ρ for Li, Na, and K vs cell volume Ω . The solid line refers to experiment (Refs. 2 and 29). The dashed and alternating dash-dot lines refer to calculations using the APW and HA pseudopotentials, respectively.

Additional values may be found plotted and tabulated elsewhere.²⁵

The corresponding derivatives

$$\frac{1}{2\pi} \int d\Omega \frac{\partial}{\partial q} S'(\vec{q}) \delta\left(\hat{q} \cdot \hat{k} + \frac{q}{2k}\right) \Big|_{k=k_F} \quad (26)$$

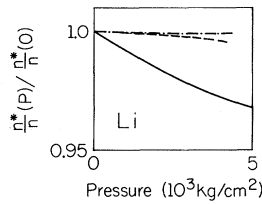


FIG. 10. Effective number of electrons per atom, n^*/n , in the Hall effect for Li, renormalized by the zero-pressure value vs pressure P . The solid line refers to experiment. The dashed and alternating dash-dot lines refer to calculations using the APW and HA pseudopotentials, respectively.

are given in Fig. 5. Tables of these derivatives for Li, Na, and K, together with more extensive figures, are given elsewhere.²⁵

IV. RESULTS

A. Thermoelectric power

The computed thermoelectric powers as functions of pressure are compared with data for Li, Na, and K in Fig. 6. Table II contains factors for converting these values to reduced thermopowers ξ . The computed partial thermopowers of Li are given in Fig. 7; corresponding curves for Na and K are reported elsewhere.²⁵ The zero-pressure results of Robinson and Dow (who neglected nonlocal and kinetic-anisotropy effects), and Bortolani and Calandra (who neglected kinetic-anisotropy), are also indicated in Fig. 6.

The agreement between theory and data for the thermopowers and their pressure dependences is pleasing—and represents a distinct improvement over previous work.^{8,9,26} Observe that the theory reproduces not only the signs of the thermopowers but their magnitudes and pressure dependences as well. The slight discrepancies between theory and data can be attributed to the approximate nature of the pseudopotentials (e.g., for Na) and structure factors used. For example, corrections to the elastic-constant structure factor

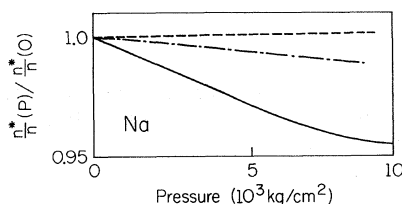


FIG. 11. Effective number of electrons per atom in the Hall effect for Na renormalized by the zero-pressure value vs pressure P . The solid line refers to experiment. The dashed and alternating dash-dot lines refer to calculations using the APW and HA pseudopotentials, respectively.

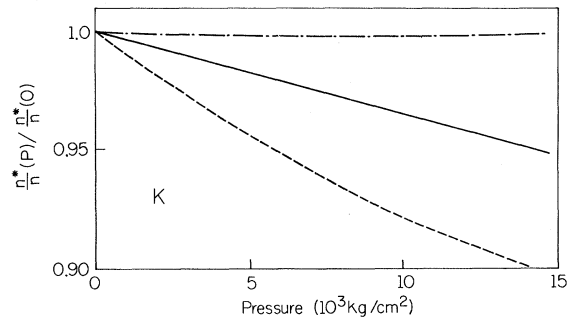


FIG. 12. Effective number of electrons per atom in the Hall effect for K renormalized by the zero-pressure value vs pressure P . The solid line refers to experiment. The dashed and alternating dash-dot lines refer to calculations using the APW and HA pseudopotentials, respectively.

model are known to produce approximately 20% corrections to the thermopower of Li, bringing the theory into even better agreement with the data.²⁷

The thermopower is dominated by scattering with momentum transfer $\hbar q \approx 2\hbar k_F$, as is demonstrated by Fig. 8, which exhibits the various terms occurring in the integrand in Eqs. (23) and (24).

B. Resistivities

The computed resistivities of Li, Na, and K (using the free-electron mass)²⁸ are shown in Fig. 9, along with data.^{2,29} The agreement between theory and experiment is gratifying: the signs of the pressure dependences are correctly reproduced; and the absolute values of the resistivities are given to within a factor of ≈ 2 , that uncertainty being directly ascribable to uncertainties in the pseudopotential (see Fig. 1).

C. Hall coefficient

The numbers of effective electrons per atom, $n^*/n = (R_H ec)^{-1}$, obtained from the Hall coefficients R_H ,³⁰ are given in Figs. 10–12 and Table III. Observe that the theory reproduces the experimental values of n^*/n at all pressures to within 15%. The discrepancies between theory and experiment are generally less than the 15% uncertainties in the pseudopotentials and structure factors. Although n^*/n measures the anisotropy of the scat-

TABLE III. n^*/n at zero pressure, experimentally (Ref. 30) and calculated using the pseudopotentials of Refs. 23 and 21 (HA and APW), respectively.

	Li	Na	K
Expt.	0.87	0.99	1.00
HA	0.78	1.00	1.00
APW	0.88	1.00	1.00

tering and is especially sensitive both to distortions of the Fermi surface (omitted in the free-electron model) and to uncertainties in the structure factor, the computations reproduce the zero pressure values of n^*/n and the correct signs (and approximate magnitudes) of the pressure derivatives $d(n^*/n)/dP$. The sole exception is the sign of $d(n^*/n)/dP$ for Na, which is correctly reproduced by the HA pseudopotential, but not by the APW pseudopotential.

V. CONCLUSIONS

The most striking conclusion of these analyses is that the high temperature thermoelectric powers of Li, Na, and K can be computed with considerable confidence as functions of pressure. Indeed, the thermopowers appear to be even less sensitive to details of the pseudopotentials than the resistivities. Nevertheless, the resistivities and Hall coefficients of these metals can likewise be computed with confidence as functions of pressure, using only elastic-constant data and published pseudopotentials. The small discrepan-

cies between theoretical and experimental values of the transport coefficients are ascribable to uncertainties in the model pseudopotentials and structure factors. We find no evidence that the microscopic theory of the mean free path [Eq. (1)] requires revision for the high temperatures considered here.³¹ The experimental data can be understood within the framework of a relaxation-time approximation solution of Boltzmann's equation.

It is noteworthy that the resistivity is dominated by lower-momentum transfer scattering processes than either the Hall coefficient (which samples the anisotropy of the scattering) or the thermopower (which is sensitive to the values of the pseudopotential and structure factor near $q \approx 2k_F$).

Our calculations suggest that two ingredients are especially helpful in producing an energy-dependent mean free path and a large thermoelectric power: (i) highly anisotropic lattice dynamics and structure factor $S'(\vec{q})$; and (ii) a pseudopotential $V(q)$ such that $\partial |V|^2 / \partial q$ is large near $q \approx 2k_F$. We speculate that these rules of thumb may be useful in the search for metals or alloys with large thermoelectric powers.

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