PHYSICAL REVIEW VOLUME 171, NUMBER 3 15 JULY 1968

Electron-Phonon Interactions in Solid Alkali Metals. I. Scattering and Transport Coefficients*

JOHN E. ROBINSON† AND JOHN D. DOW‡
Argonne National Laboratory, Argonne, Illinois

(Received 28 September 1967; revised manuscript received 29 January 1968)

Electron-phonon scattering in all the solid alkali metals at high temperature is studied in a calculation allowing detailed numerical assessment of anisotropy. The primary result sought and obtained is a conclusive accounting for the divergence of Li from the other alkali metals in having a large positive electron-diffusion thermopower. Animalu-Heine-Abarenkov pseudopotentials are used. The phonon dynamics is contained in a three-force-constant dynamical matrix fitted to elastic constants listed by Huntington, which reproduces the experimental structure factors for Na and for K to within 10% and 5%, respectively, and allows uniform treatment of all the alkalis. The electronic free path $l(\epsilon,\hat{k})$ and $\partial \ln l(\epsilon,\hat{k})/\partial \ln\epsilon$ are computed for $\hat{k}$ in the principal symmetry directions, appropriate averages giving estimates for several transport-property coefficients. The anisotropy as calculated is very marked for Li and appreciable for Na, and gives Hall coefficients in satisfactory accord with those accurately known. The thermopower coefficients ξ agree in sign and, except for Cs, semiquantitatively in magnitude with experiment, the decisive role being filled by the pseudopotentials. Estimated resistivities are, not unexpectedly, unsatisfactory. Analysis for Na, using scattering amplitudes fitted to resistivity, indicates strongly that most of such quantitative discrepancies as remain are primarily ascribable to slight but important inaccuracies in the pseudopotentials. A more thorough reinvestigation will, however, be required to account for the behavior of Cs.

I. INTRODUCTION

THE ordinary electronic transport properties of monovalent metals provide examples both of some of the earliest successes and of some of the most persistent inadequacies of solid-state theory. Bardeen's classic 1937 paper[1] convincingly demonstrated the validity of the now conventional Bloch-Wilson theory of electrical conductivity and yielded a model of the electron-phonon interaction in normal metals of truly remarkable prescience and survival value. Perhaps the outstanding and most obstinate frustration through the years has been the failure to account convincingly for the contribution of electron diffusion to the thermoelectric power. It is an old story that, while both naive physical intuition and familiar simple theory have led rather firmly to the expectation that the sign of the electron-diffusion thermopower should follow that of the Hall effect and be negative for all monovalent metals, in fact it is positive for Cu, Ag, Au, and for Li alone of the alkalis. The noble metals have had the lion's share of the attention to this puzzle, a discreet silence usually being accorded to the alkalis save to note the large magnitude of the diffusion thermopower in Li. In a preceding paper[2] it was demonstrated by one of us that a negative Hall coefficient and positive diffusion thermopower can jointly be exhibited by a free-electron gas coupled to a bath of acoustic lattice vibrations, as a result of the mean-free-path energy dependence produced purely by the core-Coulomb interference inherent in the simplest pseudopotential descendent of Bardeen's electron-ion interaction. In particular, Li was found to be so strongly differentiated in the model calculation from the other alkalis as to indicate that core-Coulomb interference dominates in differentiating the real solids, and this provided much of the motivation for the present work.

In this paper, we present the results of the simplest possible realistic calculation of the electron-diffusion thermopowers of the solid alkali metals at temperatures greater than the Debye temperature,[3] and we demonstrate that the supposedly anomalous thermopower of lithium can be fully understood within the context of the hypothesis advanced in Ref. 2. That is, the electron-diffusion thermoelectric powers of the alkali metals can be calculated with at least semiquantitative accuracy in a free-electron picture by ordinary transport theory provided that the energy dependence of the mean free path is handled carefully. In addition, we obtain values for resistivities, for mean free paths, and for the effective densities of carriers as measured in the Hall effect. A particular feature of the computations is that they

---

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

† Address during 1967–68 academic year: Istituto di Fisica dell'Universita di Pisa, Piazza Torricelli 2, Pisa, Italy.

‡ Resident Student Associate at Argonne National Laboratory during summer 1966; National Aeronautics and Space Administration Trainee, University of Rochester. Present address: Palmer Physical Laboratory, Princeton University, Princeton, N. J.

[1] J. Bardeen, Phys. Rev. **52**, 688 (1937).

[2] J. E. Robinson, Phys. Rev. **161**, 533 (1967). The viewpoint underlying the present undertaking is developed in this reference, which also contains a summary of and references to the relevant background on electron-diffusion thermopower.

To those references might here be added a number of other articles, principally by J. M. Ziman and by M. Bailyn, which deal specifically with transport coefficients in the solid alkalis, but which preceded the advent of reasonable pseudopotentials and structure factors and, at least partly because of this, have a focus and approach rather removed from those of this paper. Perhaps the part of this earlier work which makes the closest contact with ours is Bailyn's emphasis on the importance of umklapp scattering [see, e.g., Phil. Mag. **5**, 1059 (1960) and references cited therein]. Nowhere in all that hard work does there appear to have been a calculation of the diffusion thermopower really competent to test any hypotheses advanced. For example, in the article by J. G. Collins and J. M. Ziman [Proc. Roy. Soc. (London) **A263**, 531 (1961)] it is notable that *diffusion* thermopower is not even mentioned.

[3] For a preliminary account, see J. E. Robinson and J. D. Dow, Bull. Am. Phys. Soc. **12**, 22 (1967).

yield what we believe to be the first detailed exploration with a realistic scattering model of anisotropy in the contributions to the transport coefficients.

Since we wish to make consistent comparisons, our procedure is chosen so as to afford uniform treatment to all the alkalis. Accurate experimental information which is available only for some, notably for sodium, is used to check the accuracy of the procedure. It is adequate to our purposes to treat a free-electron gas coupled to the lattice vibrations in a rigid-ion approximation. The electron-ion matrix elements are taken to be the pseudopotentials calculated by Animalu, Heine, and Abarenkov (AHA).[4] Phonon dynamics is subsumed in a phenomenological dynamical matrix which is uniquely determined by elastic constants data and which reproduces known experimental structure factors (for Na and K) to well within 10%. In this way we remedy the two most serious defects of the model calculation while retaining its essential simplicity. The specific improvements are in the more realistic behavior of the AHA potentials at large momentum transfers and in using a correct distribution of vibrational states at short-wavelength and in umklapp processes.

We do not attempt or find fully quantitative agreement with experiment, which in any event does not appear attainable with presently available pseudopotentials. As was anticipated, the divergence of lithium from the other alkalis in respect of dependence of the electron-ion pseudopotential on momentum transfer is, when amplified by the phonon structure factor, sufficiently large that almost any sensible procedure would succeed in resolving the thermopower problem. Accordingly, we treat the AHA potentials as if they were local and retain only the leading term in the solution of the Boltzmann equation. Our present insistence on simplicity is also motivated by the belief that one should know the results of a "bare-bones" calculation before attacking the complications of a quantitatively definitive treatment. The major part of the quantitative failings in our numerical results could be accounted for by errors in the pseudopotentials, mostly at a level of accuracy beyond that commonly thought sufficient for band-structure calculations. It follows that a close enquiry into inherent limitations of our procedure would involve a critical study of pseudopotentials and in particular of the accuracy and reliability of practical methods for their evaluation. Such a study does not yet exist, and it would be far beyond the scope of this paper to try to provide one. Although the use of empirical pseudopotentials would appear an attractive alternative to the AHA potentials, their determination for all the alkalis is no trivial task, and we have preferred to take what we now have, concentrate on its most reliable features, and avoid adjusting the input.

The transport theory model is discussed and formal expression for the transport coefficients presented in Sec. II. Section III is reserved to a treatment of the phonon structure factor. These two sections completely specify the computations, which then contain no adjustable parameters and are carried out without numerical approximation. Our results are presented in Sec. IV, followed by a discussion in Sec. V.

II. TRANSPORT-THEORY MODEL

In recent years, variational calculations of the transport properties of metals have been in vogue because of their apparent simplicity and physical directness.[5] However, the very strong elastic anisotropy of all the solid alkalis warns us to be prepared to deal with substantial anisotropy in the electronic free path when it is limited by electron-phonon scattering. That this is a real possibility is indicated by the experimental low-field Hall coefficients, which led Deutsch, Paul, and Brooks[6] to suggest angular variations of the conductivity relaxation time by as much as a factor of three. In such circumstances, the practical advantages of a variational calculation are not so clear. There is no assurance that the standard isotropic variational expressions are adequate, and variational ratios (e.g., for the resistivity) which explicitly take anisotropy into account do not simplify sufficiently to appear advantageous. The ambiguity and uncertainty inherent in the choice of trial functions is significantly increased. Finally, examination at a microscopic level of scattering anisotropy is in a variational calculation of resistivity a bit indirect and circumscribed by the practical necessity of truncating expansions in Kubic harmonics. Therefore, we deviate from current fashion and consider working within the context of a Boltzmann equation with an anisotropic relaxation time.

We shall work in a weak-pseudopotential approximation, and note that while this implies the validity of a weak-scattering approximation[7] the converse need not be so. Specifically, we thereby imply the existence of a Boltzmann equation,[8] adequacy of the rigid-ion model with a spherically symmetric electron-ion interaction $V(q)$,[9] and that simple plane-wave electrons with kinetic energy $E(k)\sim k^2$ suffice for this calculation. It is then argued in Appendix A that at high temperature the phonon-limited mean free path $l(\mathbf{k})$ for an electron of wave vector $\mathbf{k}$ is to a satisfactory approximation given by Eqs. (A21) and (A22):

$$\frac{1}{l(\mathbf{k})}=\frac{\Omega_0 m^2}{4\pi\hbar^4 k^4}\int_0^{2k} dq\, q^3 |V(q)|^2 S(\hat{k},q)\,, \tag{1}$$

---

[4] A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).

[5] See, e.g., J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1962), Chaps. VII and IX.

[6] T. Deutsch, W. Paul, and H. Brooks, Phys. Rev. **124**, 753 (1961).

[7] M. Greene and W. Kohn, Phys. Rev. **137**, A513 (1965).

[8] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

[9] See, e.g., L. J. Sham and J. M. Ziman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15.

where we have defined $S(\hat{k},q)$ by

$$S(\hat{k},q)\equiv(1/2\pi)\int d\Omega(\hat{q})S'(\mathbf{q})\delta[\hat{q}\cdot\hat{k}+(q/2k)]. \qquad (2)$$

Here Ω_0 is the ionic volume, m the electronic effective mass, $S'(\mathbf{q})$ the static-structure factor[10] less the Bragg reflection peaks, $d\Omega(\hat{q})$ an element of solid angle about $\hat{q}$, and $\hbar\mathbf{q}$ is of course the crystal momentum transfer in a scattering event. In the present scattering model all anisotropy arises, through $S(\hat{k},q)$, from the lattice vibrations. Some commonly used expressions for the electrical resistivity[11,12] are proportional to the average of Eq. (1) over $\hat{k}$ and clearly are incorrect in the presence of anisotropic scattering: Their use would be tantamount to adding the resistivities rather than the conductivities of the branches of a parallel circuit. Equation (1) is of course just what would have been found from a Fermi "golden rule" calculation of the momentum-transfer cross section. Here, however, it has been obtained as the dominant term, thanks primarily to cubic symmetry, of the solution to a Boltzmann equation with an anisotropic relaxation time.

For $V(q)$ we use the Animalu, Heine, Abarenkov[4] (AHA) pseudopotentials as tabulated in Harrison's[13] book. These values are adequate to allow us to establish our main results, to a considerable extent because the difference between Lithium and the other alkalis is so great that a fully quantitative calculation is not in fact required. Using them to calculate a few transport coefficients selected for qualitatively different sensitivities to the input can provide cross checks on the reliability of the results. Derivatives of $V(q)=\langle\mathbf{k}+\mathbf{q}|V|\mathbf{k}\rangle$ with respect to k are, presumably, appreciably more sensitive than are the values themselves to approximating pseudo wave functions by single plane waves. In addition, in just those instances in which the largest k dependence is to be expected, the procedure used to evaluate the $V(q)$ is least apt to be accurate. This is reflected in calculated band-structure effective masses at the Fermi surface, which are generally regarded with some distrust even if the $V(q)$ are adequate to give band gaps with tolerable accuracy. We shall here use the values available for $V(q)$ but neglect any explicit k dependence at finite q, and it is in this sense that we treat the pseudopotentials as if they were local. This can, for the heavier alkalis particularly, result in quantitative errors in the thermopower, but of course has no effect at all on the mean free path or Hall coefficient. Evaluation of the static-structure factor poses a considerable problem, since accurate computations of $S'(q)$ do not yet exist and satisfactory experimental data are available only for Na [14] and K.[15] In order to provide uniform treatment to all the alkalis, we are forced to rely on what knowledge of the phonon dynamics can be extracted from macroscopic elastic constants. Our procedure for approximating to $S'(q)$ is discussed in the next section.

The relevant transport coefficients may be expressed as functionals of the electronic mean free path in the usual manner. Since we are interested in anisotropy at the microscopic level our first concern is to calculate directly microscopic contributions to the bulk coefficients, and we shall refer to these as partial, or microscopic, coefficients. We define a partial thermopower coefficient $\xi(\hat{k})$ by

$$\xi(\hat{k})\equiv1+[d\ln l(\mathbf{k})/d\ln E(\mathbf{k})]_{|\mathbf{k}|=k_F}, \qquad (3)$$

and a partial resistivity $r(\hat{k})$ by

$$r(\hat{k})\equiv(\hbar k_F/ne^2)(1/l(\hat{k})), \qquad (4)$$

where we have written

$$l(\hat{k})\equiv l(\mathbf{k})\,|_{|\mathbf{k}|=k_F}. \qquad (5)$$

In Eqs. (3)–(5), k_F is the Fermi wave vector an n the mean carrier density.

In differentiating Eq. (1) to get $\xi(\hat{k})$ there are three sources of energy dependence to consider: the q dependence of the integrand, the k dependence of $V(q)$ (which we have chosen to neglect here), and, purely because of the elastic anisotropy, $S(\hat{k},q)$. The primary effect of including $(dS(\hat{k},q)/dE_k)$ would be to reduce slightly the anisotropy of the calculated $\xi(\hat{k})$. We shall take into account only the q dependence. Macroscopic transport coefficients can then be computed from Eqs. (1)–(5) as if $\hat{k}$ were the carrier group label in a many-band model.[16,17] The usual integrals over the Fermi surface[18] may be replaced by sums over $\hat{k}$, remembering that the element of area is here independent of $\hat{k}$. We then have for the electron-diffusion thermopower

$$S_{\text{diffusion}}=-[\tfrac{1}{3}(\pi^2k_B{}^2T)|e|E_F]\xi_{\text{av}}, \qquad (6)$$

$$\xi_{\text{av}}\equiv(\sum_{\hat{k}}l(\hat{k}))^{-1}\sum_{\hat{k}}l(\hat{k})\xi(\hat{k}). \qquad (7)$$

The resistivity is

$$\rho=r_{\text{av}}\equiv(\sum_{\hat{k}})[\sum_{\hat{k}}(1/r(\hat{k}))]^{-1}. \qquad (8)$$

The effective density of charge carriers n^* defined by writing the Hall coefficient as $R=-(1/n^*|e|c)$ is given by

$$(n^*/n)=\{(\sum_{\hat{k}}l(\hat{k}))^2/(\sum_{\hat{k}}l^2(\hat{k}))\}\leqslant1. \qquad (9)$$

---

[10] See in Appendix A, Eqs. (A8) and (A18).

[11] G. Baym, Phys. Rev. **135**, A1691 (1964).

[12] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966), Sec. 4.1.

[13] Reference 12, p. 309 ff.

[14] A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. **128**, 1112 (1962).

[15] R. A. Cowley, A. D. B. Woods, and G. Dolling, Phys. Rev. **150**, 487 (1966).

[16] Reference 2, Sec. II.

[17] A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1953), 2nd. ed., Sec. 8.42.

[18] See, e.g., Ref. 5, Chap. VII.

In computations of the macroscopic coefficients it has been quite common, for practical reasons, to simplify at least the integrations associated with umklapp processes, and the numerical errors so introduced are difficult to assess.[19] Such uncontrolled numerical approximations are completely avoided in calculation of the microscopic coefficients $l(\hat{k})$ and $\xi(\hat{k})$. This circumstance is worth emphasizing in view of the considerable notoriety for sensitivity to details of calculation ascribed, e.g., to the diffusion thermopower.

III. PHONON STRUCTURE FACTOR

The dynamical structure factor, which is proportional to the differential scattering cross section per unit energy, can be easily extracted from neutron-bombardment data.[20] Unfortunately, the only alkali metals for which such data presently exist are sodium[14] and potassium,[15] and the structure factors for the other alkalis must be approximated using elasticity data. One of the notable deficiencies of such an approximation is that the elastic data contain information about only the long-wavelength phonon dynamics, so that one would expect any model based on elastic constants to break down for short-wavelength phonons. This difficulty is most serious for momentum transfers near the phonon zone boundary ($(q/2k_F)\approx 0.63$ in the alkalis), but disappears for $\mathbf{q}$'s approaching reciprocal lattice points since there the *reduced* phonon *wave vector* again tends to zero. This latter circumstance is important because it allows us to fit $S(\mathbf{q})$ where it is largest, near Bragg points, as well as near $\mathbf{q}=0$ and, in effect, to interpolate through short *wavelength* regions. We now discuss our method for determining from long-wavelength data an approximate structure factor satisfactory at all wavelengths. We limit discussion to cases in which the phonons may be regarded as if in thermal equilibrium since we are not here concerned with phonon drag, and further take the harmonic approximation to be adequate for fixed temperature. The space and time Fourier transform $S(\mathbf{q},\omega)$ of the ions's pair correlation function may then be expressed in terms of the frequencies $\omega_p(\mathbf{q})$ and polarization vectors $\hat{\epsilon}_p(\mathbf{q})$ of the harmonic lattice, and in the one-phonon approximation[7,20,21] we have

$$S'(\mathbf{q},\omega)=\frac{\hbar}{2M}\sum_{1=p}^{3}\frac{[\mathbf{q}\cdot\hat{\epsilon}_p(\mathbf{q})]^2}{\omega[\exp(\beta\hbar\omega)-1]}\times\{\delta[\omega-\omega_p(\mathbf{q})]+\delta[\omega+\omega_p(\mathbf{q})]\}. \quad (10)$$

Here p is the polarization index, M the ionic mass, $\beta=(1/k_BT)$, and the prime indicates that the Bragg reflections associated with the static lattice have been omitted, as have anharmonic terms. Since the scattering of electrons is quasi-elastic, for temperatures above the Debye temperature, the $S'(\mathbf{q},\omega)$ we shall need is

$$S'(\mathbf{q},\hbar^{-1}[E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}])=\delta(\hbar^{-1}[E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}])\times(k_BT/M)\sum_{p=1}\omega_p^{-2}(\mathbf{q})[\mathbf{q}\cdot\hat{\epsilon}_p(\mathbf{q})]^2. \quad (11)$$

Since the orthogonal matrix of polarization vectors diagonalizes the dynamical matrix $D(\mathbf{q})$,[22] where

$$D(\mathbf{q})\cdot\hat{\epsilon}_p(\mathbf{q})=\omega_p^2(\mathbf{q})\hat{\epsilon}_p(\mathbf{q}), \quad (12)$$

we may use the more compact form

$$\hbar^{-1}S'(\mathbf{q},\hbar^{-1}[E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}])=[(k_BT/M)\mathbf{q}\cdot D^{-1}(\mathbf{q})\cdot\mathbf{q}]\delta(E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}). \quad (13)$$

The quantity in square brackets is the desired structure factor $S'(\mathbf{q})$. Thus, the high-temperature static-structure factor can be evaluated directly from the dynamical matrix, once the latter is determined. It is in principle unnecessary to compute even a single phonon frequency or polarization vector: What is required is the quadratic form $\mathbf{q}\cdot D^{-1}(\mathbf{q})\cdot\mathbf{q}$, and solution of the phonon eigenvalue problem is only one route to its evaluation.

Considerable effort has been devoted over the years to study of the dynamical matrix.[23] Since we shall attempt to construct it from long-wavelength elastic constants data, the anisotropic-dispersive-continuum model[24,25] immediately becomes a candidate for the attempt. In this model the frequencies for the real crystal, $\omega_p(\mathbf{q})$, are taken to differ from those of the corresponding continuum, $\omega_p'(\mathbf{q})$, by slowly varying dispersion factors $f_p(\mathbf{q})$:

$$\omega_p(\mathbf{q})=f_p(\mathbf{q})\omega_p^0(\mathbf{q}),\quad \lim_{|\mathbf{q}|\to 0}f_p(\mathbf{q})=1. \quad (14)$$

However, all simple analytic choices of dispersion factors $f_p(\mathbf{q})$ are unrealistic: Experimental dispersion relations for Na and K indicate a strong polarization dependence, and spherically symmetric choices of $f_p(\mathbf{q})$ are undesirable since they force us to sacrifice the advantages of built-in crystal symmetry and to replace the Brillouin zone with a Debye sphere, thereby making umklapp processes difficult to handle. On the other hand, it can be shown that functions $f_p(\mathbf{q})$ with full point group symmetry exist and give the exact dispersion relations whenever the polarization vectors of the crystal are independent of the magnitude of $\mathbf{q}$—a condition that ought to be approximately satisfied. But the determination of these analytically complicated functions is sufficiently difficult to render a description of

---

[19] We hasten to add that this is not done in more recent computations such as, e.g., that of Ref. 7.

[20] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[21] N. Wiser, Phys. Rev. **143**, 393 (1966).

[22] See, e.g., the excellent summary in Sec. 2 of S. H. Vosko, R. Taylor, and K. H. Keech, Can. J. Phys. **43**, 1187 (1965).

[23] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954); A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

[24] Reference 5, Chap. I, Sec. II.

[25] K. C. Sharma and S. K. Joshi, Phys. Rev. **132**, 559 (1963); **140**, A1799 (1965).

the phonons in terms of an anisotropic-dispersive-continuum model inappropriate.

The neutron-scattering data for Na and K indicate that the solid alkalis have predominantly short-range elastic forces; this suggests that a Born–von Kármán force-constant model will provide a rapidly convergent treatment of the lattice dynamics. In addition, the Born–von Kármán dynamical matrix has the desired full Brillouin-zone symmetry and **q**-space periodicity, which helps to reduce the short-wavelength inaccuracies introduced by the elastic-constant approximation and, further, automatically takes care of the otherwise cumbersome unklapp processes.[7] Woods *et al.*[14] and Cowley *et al.*[15] have interpreted their scattering results in terms of such a model and have published force-constant matrices for the first five shells of nearest neighbors. Of these interatomic force constants, the first three [$\phi_{xx}^1(111)$, $\phi_{xy}^1(111)$, and $\phi_{xx}^2(200)$] are very much larger than the rest. Therefore, reasonable approximations to the structure factors and the dynamical matrices can be obtained from a three-force-constant Born–van Kármán model. We have performed detailed numerical calculations for Na and K to confirm this hypothesis and find that neglect of the other force constants introduces a ***maximum*** error in the structure factor of about 10% for Na and of about 5% for K. The errors caused by elastic-constant approximation to the structure factors of the remaining alkalis should be correspondingly small. {*Note added in proof.* Very recently, preliminary neutron scattering results for the phonon dispersion curves in Li have been reported by H. G. Smith, G. Dolling, R. M. Nicklow, P. R. Vijayaraghavan, and M. K. Wilkinson [Bull Am. Phys. Soc. **13**, 451 (1968)]. The LA mode in the [110] direction shows clearly the influence of long range forces and the interatomic force constants are non-negligible out through sixth neighbors, but the first-neighbor force constants are nevertheless by *far* the largest. We have not made detailed calculations using these new neutron data, but we have checked the frequencies given by the elastic constants dynamical matrix at the zone boundaries, where one might expect our procedure to be *least* accurate. As compared to the experimental values, the frequencies used in our calculations for Li are 13% low at the point *P* in the [111] direction and 8% low in the [100] direction at *H*. At *N* in the [110] direction, our values are, for all three branches, including the low Σ_2 mode, in agreement with the neutron results to within the stated experimental errors.}

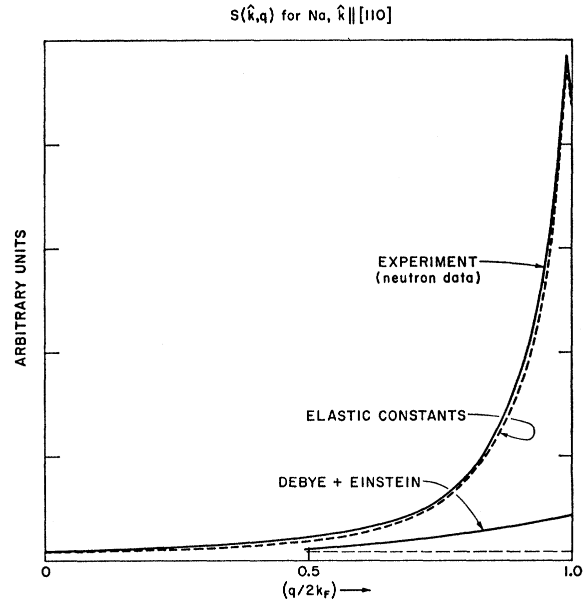

FIG. 1. Effect of symmetry on the structure factor for Na. $S(\hat{k},q)$, Eq. (2), for the [110] direction and for $S'(\mathbf{q})$ obtained, as indicated in the figure, from the five neighbor thirteen force constant fit to neutron-diffraction data (Ref. 14), from the two neighbor three-force-constant fit to the elastic constants, from the elastic-continuum limit $S'(\mathbf{q})=S'(0)=\text{constant}$, and from taking the phonon frequency to be nondispersive out to the Debye limiting wave number and constant thereafter (Ref. 32). Only the large q parts of the curves in the latter two cases are shown.

In our computations we have used the elastic constants tabulated by Huntington[26] and have calculated the three largest force constants and the approximate Born–von Kármán dynamical matrix with the help of equations written by Squires.[27] Squires's expressions for the elastic constants and the dynamical matrix are included in Appendix B since they are especially well suited for numerical calculations.

A proposal to use a three-constant dynamical matrix for a good metal is very apt to provoke an initial apprehension that this ignores the long-range behavior of the interacting electron gas. We note first of all that our procedure is quite compatible with the existence of strong electronic influence on phonon-dispersion curves. For example, surely the most drastic of all electronic effects is the reduction of the longitudinal mode frequency at infinite wavelength from the ion-plasma frequency to zero. Further, in instances in which transverse mode frequencies are strongly reduced from those given by the direct ion-core interaction plus rigid neutralizing background, the reduction is in fact already large at the smallest wave number for which neutron data exist and is reflected in a substantial reduction of the great elastic anisotropy which would result from the direct ion-core interaction acting alone.[28] The striking elastic anisotropy of all the alkalis suggests that, aside from screening the long-wavelength longitudinal mode, the electronic contribution to the effective ion-ion interaction may be weak in *all* of them, not just in sodium and potassium.

---

[26] H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7.

[27] G. L. Squires, Arkiv Fysik **25**, 21 (1963).

[28] Compare, for example, the entries in Tables V–XIII of Ref. 22 for the direct ion-core squared frequencies ω_d^2 with the experimental ω_{expt}^2. The ratio in the acoustic limit of the two transverse mode squared frequencies, the usual anisotropy parameter, is sufficiently well given for illustrative purposes by the values for the longest wavelengths occurring in the tables.

TABLE I. Thermopower coefficients ξ for the alkali metals at room temperature. The partial thermopower coefficients calculated for each of the three symmetry directions using a structure factor constructed from elastic constant data are denoted by ξ_k; the appropriate average of these values is ξ_{av}. The quantity ξ_{Debye} is the average value obtained when the phonon structure factor is approximated in the Debye limit $S_{\text{Debye}}(\mathbf{q})=S(0)$. The experimental thermopower coefficient is ξ_{expt}. See text for details.

	ξ_k			ξ_{Debye}	ξ_{av}	ξ_{expt}	
k:	[100]	[110]	[111]				
Li	−1.89	−6.24	−3.02	−0.96	−3.49	−6.7[a]	−6.9[b]
Na	+2.24	−0.44	+0.83	+2.76	+0.65	+2.7[a]	2.7[b]
K	+2.80	+2.03	+2.35	+2.94	+2.31	+3.8[a]	4.0[b]
Rb	+2.93	+2.63	+2.74	+2.98	+2.74	+2.3[a]	
Cs	+2.90	+2.46	+2.65	+2.97	+2.62	+0.2[a]	

[a] J. S. Dugdale, Science **134**, 77 (1961).
[b] P. W. Kendall, Bull. Am. Phys. Soc. **11**, 74 (1966); and (private communication).

TABLE II. Resistivities of the alkali metals at 273°K (in units of $\mu\Omega$ cm) and the calculated average mean free paths for electrons l_{av} (in Å). The quantities r_k are the calculated partial resistivities; r_{av} is the appropriately weighted average; and r_{Debye} is the value obtained in the Debye approximation to the phonon distribution. These are to be compared with the experimental values r_{expt}.

	r_k			r_{Debye}	l_{av}	r_{av}	r_{expt}[a]
k:	[100]	[110]	[111]				
Li	6.77	20.33	18.50	1.09	72.4	13.62	8.55
Na	1.99	2.38	2.24	0.73	659	2.23	4.3
K	1.98	2.13	2.10	0.80	1057	2.08	6.1
Rb	2.22	2.29	2.24	0.90	1114	2.25	11.6
Cs	2.17	2.22	2.18	0.94	1341	2.20	19

[a] Experimental numbers are taken from *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., Cleveland, Ohio, 1959), 40th ed.

Prominent long-range interionic forces in simple metals would seem to be correlated with strong reduction by screening of phonon frequencies at large wave number from those of a Coulomb lattice.[29,30] However, when such is the case, one would expect to see the Kohn anomalies,[30] and it should be recalled that experimental detection of an unambiguous Kohn effect has proved both rare and difficult.[31] Accordingly, we may provisionally regard as secondary, at least for the alkalis, electronic effects which cannot be subsumed in the elastic constants. In contrast, it is essential that the lattice symmetry be properly incorporated in the dynamical matrix if a reasonable structure factor is to be obtained. Physically this is because it is just the quasi-periodicity of the vibrating lattice which is responsible for the great rise of $S'(\mathbf{q})$ in the diffuse scattering peaks centered on the Bragg reflections. Formally, this is clear from Eq. (11) since $\hat{\epsilon}_p(\mathbf{q})$ and $\omega_p(\mathbf{q})$ are periodic in $\mathbf{q}$ and the latter vanishes at reciprocal lattice points. The effect of symmetry on calculated $S(\hat{k},q)$ is illustrated in Fig. 1. For an elastic continuum, $S(\mathbf{q})$ is of course independent of $|\mathbf{q}|$.[2] Another simplified model which has occasionally been adopted[1,31] in the past consists in approximating $\omega_p(\mathbf{q})$ by the continuum form $\omega_p^{(0)}(\mathbf{q})$ for q less than the Debye wave vector q_0 and by the constant $\omega_p^{(0)}(\mathbf{q}_0)$ for q greater than q_0.[32] Both of these models wretchedly misrepresent the structure factor in the umklapp region.

It seems clear that the three-force-constant $D(\mathbf{q})$ is sufficient for our purpose, namely to provide reliable numbers for transport calculations in the alkalis. Effort expended in the absence of neutron data to secure greater accuracy in $D(\mathbf{q})$, say 1%, would be misplaced in view of our other approximations and of the uncertainties in presently available pseudopotentials.

IV. NUMERICAL RESULTS AND COMPARISON TO EXPERIMENT

In Tables I–III are collected our calculated values for thermopower, resistivity, mean free path, and the effective number of carriers together with the best available experimental values. For the effective masses required we have used the values listed in Table 4 of Animalu and Heine,[4,33] and measured lattice constants have been used: There are no adjustable parameters in these calculations. Values of $V(q)$ at sufficiently small intervals of $(q/2k_F)$ were obtained by parabolic interpolation of those published by Animalu and Heine,[4,18] and the differentiation in Eq. (3) was of course done analytically. Averages over the entire Fermi surface were judged to require more labor than is warranted by the accuracy of our input data and were not made. Instead, we have computed the partial coefficients $\xi(\hat{k})$, $l(\hat{k})$ without any numerical approximation for

TABLE III. Effective number of charge carriers per electron, n^*/n, for the solid alkali metals at room temperature.

	Li	Na	K	Rb	Cs
Calculated	0.77	0.99	1.00	1.00	1.00
Experiment	0.87[a]	0.95[a]	0.95[a]	0.94[b]	0.98[c]
	0.79[d]	1.17[c]	1.11[c]		

[a] T. Deutsch, W. Paul, and H. Brooks, Phys. Rev. **124**, 753 (1961).
[b] E. Krautz, Z. Naturforsch. **5a**, 13 (1958).
[c] F. J. Studer and W. D. Williams, Phys. Rev. **47**, 291 (1935).
[d] A. v. Ettingshausen and W. Nernst, Ann. Physik **29**, 343 (1886).

---

[29] See, e.g., B. N. Brockhouse, in *Phonons and Phonon Interactions*, edited by T. A. Bak (W. A. Benjamin, Inc., New York, 1964), p. 261.

[30] Reference 22, Sec. 5, especially pages 1225–7, 1241–2.

[31] E. J. Woll, Jr. and W. Kohn, Phys. Rev. **126**, 1693 (1962); see also Ref. 22, pp. 1228–9, 1235, and as cited in Ref. 29.

[32] Reference 1; also D. Simkin, Ph.D. dissertation, University of Illinois, 1963 (unpublished) (copy available from University Microfilms, Inc., Ann Arbor, Mich.). The velocity of sound given by the elastic constants was used in Fig. 1, while in practice the velocity of sound used in a Debye-plus-Einstein model is chosen differently, e.g., to give a Debye temperature.

[33] These are the masses stated to have been used in computing the model pseudopotentials, and differ by insignificant amounts from the Fermi surface density of states masses calculated by Animalu and Heine and listed in Table 6 of Ref. 4. The interested reader will note a number of discrepancies between the masses listed in Tables 4 and 6 of Ref. 4 which are attributed to Ham and the values listed by Ham [Phys. Rev. **128**, 2524 (1962), Tables III–V]. {*Note added in proof.* D. Weaire [Proc. Phys. Soc. (London) **92**, 956 (1967)] has recalculated the Fermi surface masses, correcting some errors in the results of Ref. 4. These "Hartree masses" still differ appreciably from Ham's calculated results, and we have not made use of them.}

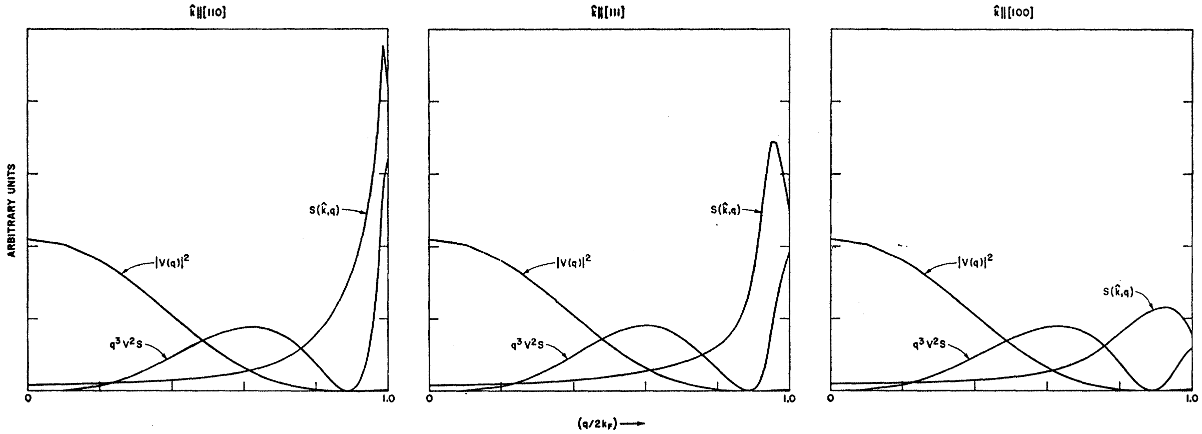

FIG. 2. Mean free path integrand factors for Na. Computed for the principal symmetry directions using $S'(q)$ as obtained from the three-force-constant dynamical matrix. Scale factors for different integrand factors are not the same.

each of the three principal symmetry directions, and then have averaged these values over the symmetry directions according to Eqs. (7)–(9), weighting each direction by the number of times it occurs in the star of the wave vector.

On the whole the numerical results have a quite pleasing aspect, and the sources of the outstanding quantitative discrepancies with experiment can be pinpointed or plausibly identified. We preface our detailed comments by two remarks: Firstly, the mean free path (and hence the resistivity) is explicitly sensitive to the value of the band mass through the m^2 factor in Eq. (1), while neither the thermopower nor (n^*/n) is since the mass cancels out in Eq. (3) and Eq. (9). Secondly, the pseudopotential exerts an over-all control on the end results by limiting the effectiveness with which the rise of $S(\hat{k},q)$ toward the first Bragg peak can augment the scattering. This can be seen rather clearly by plotting $|V(q)|^2$, $S(\hat{k},q)$, and the integrand $q^3|V(q)|^2S(\hat{k},q)$ of Eq. (1), and in Figs. 2–4 we present a number of such plots for reference.

The hoary old problem of the electron-diffusion thermopower of solid Li can be considered fully resolved. In particular, the qualitative differences between Li and the rest of the alkalis are definitely accounted for, and the value $\xi_{110}=-6.24$ suggests that quantitative agreement with experiment can be obtained by slightly modifying our treatment. The decisive role is played by the pseudopotential, which for Li exhibits moderately strong Coulomb-core interference and is much larger at $q=2k_F$ than for the other alkalis. Indeed, the reversed sign in ξ_{av} is obtained even when a Debye structure factor is used, without any umklapp enhancement at all. As expected, the extreme elastic anisotropy of Li is mirrored in the thermopower.

The discrepancy between calculated and measured ξ for Na, while initially disturbing, can be accounted for convincingly, and will be discussed shortly. We have little to say on the contribution of the explicit k dependence of the pseudopotentials. For lithium it would appear to give a positive increment to ξ, perhaps of about one or somewhat more but in any event quite a bit smaller in magnitude than the contribution of the q dependence, and for sodium it would appear to have little effect. These statements represent rather rough estimates rather than a detailed calculation. They can however also be supported by using the recent phase shift calculations of Meyer *et al.*[34] As regards K, Rb, and Cs we note first of all that $V(q)$ is so small in the range of the largest elastic momentum transfers as nearly to emasculate the peak in $S(\hat{k},q)$. For a $V(q)$ independent of E_k $\xi\leqslant 3$, and the experimental data therefore indicate that explicit k dependence is important in potassium. Moreover, the recent determination by Lee and Falicov[35] of the potassium pseudopotential has shown nonlocality to be more significant than the AHA calculations might indicate. One expects that modifying our calculations so as to use their pseudopotential would produce substantial agreement with experiment. The thermopower predicted for Cs is by an order of magnitude too large, which we believe to be primarily due to inadequate accounting in the AHA pseudopotential for the d band above the Fermi level.[2,34] Inclusion of nonlocal screening and of spin-orbit coupling [36] in the AHA potentials leads, we find, to changes only of order 1% from our tabulated results. Fermi surface distortion can hardly be overly important since for liquid Cs $\xi=1.3$.[37] [*Note added in proof.* V. Bortolani

---

[34] A. Meyer, C. W. Nestor, Jr., and W. H. Young, Proc. Phys. Soc. (London) **92**, 446 (1967); J. M. Dickey, A. Meyer, and W. H. Young, *ibid.* **92**, 460 (1967). See especially Fig. 15 and Table 2 of the second article; and for a comparison of their scattering amplitude for lithium to that of AHA, Fig. 5(a) of the first article. Note that Debye structure factors have been used in these calculations. It is of particular interest that these authors, using an Austin form of pseudopotential, find for Cs a moderately pronounced d-state resonance (see Fig. 4 of the first article).

[35] M. J. G. Lee and L. M. Falicov, Proc. Roy. Soc. (London) **A304**, 319 (1968).

[36] A. O. E. Animalu, Phil. Mag. **11**, 379 (1965); **13**, 53 (1966).

[37] N. E. Cusack, Repts. Progr. Phys. **26**, 361 (1963).

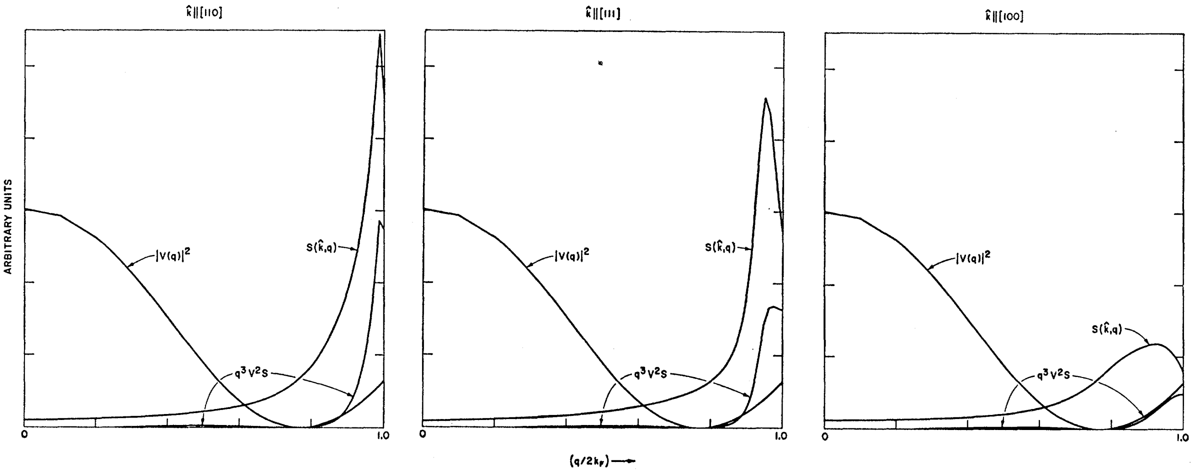

FIG. 3. Mean free path integrand factors for Li. Computed for the principal symmetry directions using $S'(\mathbf{q})$ as obtained from the three-force-constant dynamical matrix. Scale factors for different quantities differ. $q^3V^2(q)S(\hat{k},q)$ for the [100] direction is scaled up by a factor of five relative to the same quantity as plotted for the [110] and [111] directions.

and C. Calandra (private communication) have now completed a detailed calculation of the thermopower coefficients in which the contribution of the explicit k-dependence of the AHA potentials is included. Their results for Li, Na, and K are in close accord with our comments above. They obtain contributions from the k-dependence to the ξ for Rb and Cs which are *positive* and very large. The seeming agreement with ξ_{exp} for Rb in Table I is completely ruined and is therefore spurious, and the already large discrepancy for Cs is increased by more than a factor of 2.]

The agreement between calculated and measured resistivities is poor, perhaps disturbingly so. While our calculations seem to account for the unusually large resistivity of Li, they fail to explain the even larger resistivities of Rb and Cs. The smallness of r_{av} for Na, K, Rb, and Cs is clearly due to the near vanishing of $V(q)$ near $2k_F$. [As a historical remark, one may note that if $V(2k_F)$ were not in reality small, then Bardeen's 1937 calculation[1] would have been jeopardized by its use of a "Debye-plus-Einstein" phonon spectrum.]

Responsibility for the discrepancies is also attributable in part to the sensitivity to the band-structure masses, which are not very reliably known, and this circumstance in turn makes the pseudopotential's share in the errors difficult to assess. This m^2 sensitivity furnishes no refuge from the factor of two error in the resistivity of sodium, however, since there the band mass is to all present intents and purposes equal to the free-electron mass.

In the case of sodium, the quantitative disagreements with experiment can be pinned down rather neatly. Greene[7] and Kohn have given two partial wave scattering amplitudes, both of which conform to the Friedel sum rule and are fitted to give the correct resistivity. From these we construct two local pseudopotentials and then use the accurate (e.g., neutron determined) $S(\hat{k},q)$ in obtaining ξ. The amplitude which is close to that estimated by Greene and Kohn by direct calculation (their f_A) leads to $\xi \approx 2.1$, which is substantially in agreement with the experimental value 2.7. In contrast, the other amplitude (their f_B) leads to $\xi \approx -0.6$ and should be discarded on that account. As shown in Fig. 5, these two pseudopotentials and that of AHA generally differ one from another only by amounts comparable to the estimated error of 0.01 Ry in the AHA calculations. However, the unsatisfactory Greene-Kohn amplitude and the AHA potential give weak Coulomb-core interference minima in $|V^2(q)|$ which are magnified by the structure-factor peak. The sensitivity of thermopower coefficients to such amplified interference effects is also illustrated by comparison of ξ_{110} to ξ_{Debye} for lithium and sodium in Table I. Accordingly, the pseudopotential stands convicted of the error in ξ_{av} for Na listed in Table I.

The only presently available experimental check on the calculated microscopic anisotropy of the electron-phonon scattering is through the Hall effect, and the comparison of computed and empirical values of (n^*/n) given in Table III is comforting. Once again lithium is singled out as unusual, and the calculated values for the other alkalis lie within experimental error (7% for Deutsch, Paul, and Brooks[6]). Discrimination by the pseudopotential is especially marked here, since the structure factors would otherwise lead to strongly anisotropic scattering in all the alkalis.

As one final check we have repeated all calculations for Na and K using the accurate structure factors constructed from neutron-diffraction data, and in Table IV compare these results with those obtained using the three-parameter elastic-constants approximation to $D(\mathbf{q})$. We conclude that the differences between these two sets of values are for the most part negligible and never significant.

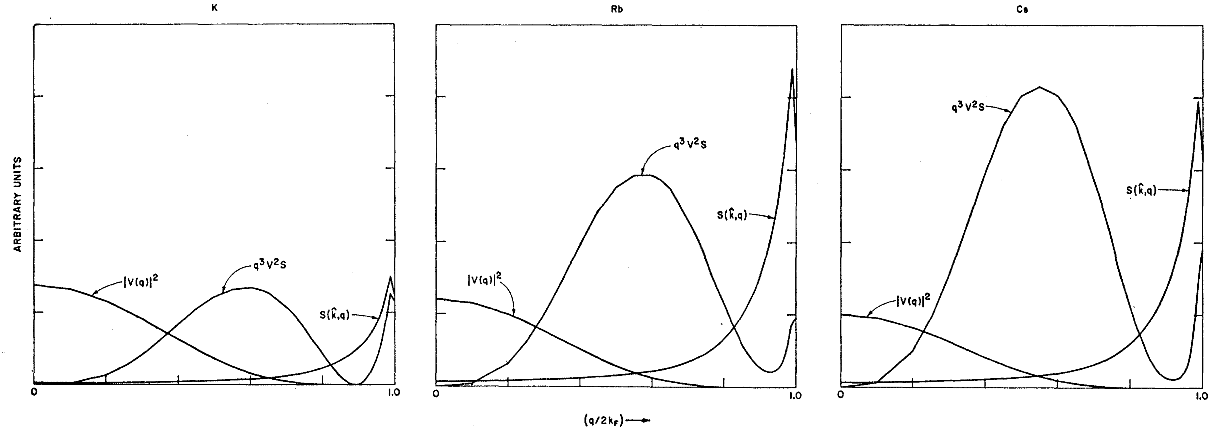

FIG. 4. Mean-free-path integrand factors for K, Rb, and Cs. Computed for the [110] direction using the $S'(\mathbf{q})$ obtained from the three-force-constant dynamical matrix. Scale factors for different quantities differ. $S(\hat{k},q)$ for Cs is scaled down by a factor of 2 relative to the plots for K and Rb.

V. DISCUSSION

The calculations herein presented have been performed in the simplest model of the solid alkali metals which incorporates what we judged to be essential to a meaningful calculation of their ordinary transport coefficients. It remains to recall and comment on some of the principal approximations in the treatment. We believe that the two most important sources of error in our numerical results are inadequacies of the AHA pseudopotentials (treated as local) and of the uncertain band masses, and that while these are not serious enough to vitiate our main claims they do largely obscure and frustrate estimates of the quantitative effects of other sins of omission and comission.[38]

Regarding use of a free electron $E(\mathbf{k})$, one may remark first that de Haas–van Alphen experiments show the Fermi surface of all the alkalis save lithium to be spherical to within 1%.[39] Nonparabolicity of $E(\mathbf{k})$ would be contained in the band masses and is otherwise of secondary importance in this calculation. Taylor, Moore, and Vosko[40] have in a careful and very detailed calculation shown that a one-OPW wave function is remarkably good for sodium, and although there is no guarantee that this is so for the other alkalis, we do not expect the use of single plane waves to have introduced any significant error in our results for K, Rb, and Cs. Positron annihilation[41] indicates an anisotropy of about 5% in the Fermi surface of lithium, with $k_{110} > k_{100}$,

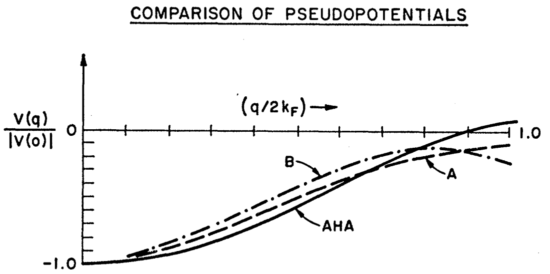

FIG. 5. Comparison of local pseudopotentials for Na. AHA denotes the local pseudopotential calculated by Animalu and Heine (Ref. 4) as tabulated by Harrison (Ref. 12). A and B denote the local potentials corresponding to the Greene and Kohn (Ref. 7) scattering amplitudes f_A and f_B. The estimated error in the AHA calculations is about one abscissa scale division.

TABLE IV. Comparison of thermoelectric power coefficients, resistivities, mean free paths, and effective number of charge carriers per electron as calculated using an elastic-constant approximation to the phonon structure factor with those calculated using neutron-diffraction data (Refs. 14 and 15). Notation is the same as in Tables I–III. See text for details.

	Na		K	
	Elasticity data	Neutron data	Elasticity data	Neutron data
ξ_{100}	+2.24	+2.22	+2.80	+2.81
ξ_{110}	−0.44	−0.24	+2.03	+2.04
ξ_{111}	+0.83	+0.60	+2.35	+2.38
ξ_{av}	+0.65	+0.66	+2.31	+2.33
ξ_{expt}	2.7[a,b]		3.8,[a] 4.0[b]	
r_{100} ($\mu\Omega$ cm)	1.99	2.14	1.98	1.92
r_{110} ($\mu\Omega$ cm)	2.38	2.56	2.13	2.09
r_{111} ($\mu\Omega$ cm)	2.24	2.48	2.10	2.03
r_{av} ($\mu\Omega$ cm)	2.23	2.43	2.08	2.03
r_{expt} ($\mu\Omega$ cm)	4.27[c]		6.10[c]	
l_{av}	659	607	1057	1085
n^*/n (calc.)	0.99	0.99	1.00	1.00
n^*/n (expt.)	0.95,[d] 1.17[e]		0.95,[d] 1.11[e]	

[a] J. S. Dugdale, Science **134**, 77 (1961).
[b] P. W. Kendall, Bull. Am. Phys. Soc. **11**, 74 (1966); and (private communication).
[c] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., Cleveland, Ohio, 1959), 40th ed.
[d] T. Deutsch, W. Paul, and H. Brooks, Phys. Rev. **124**, 753 (1961).
[e] F. J. Studer and W. D. Williams, Phys. Rev. **47**, 291 (1935).

---

[38] We do not intend here to become embroiled in or to comment on the current controversy regarding validity of the first Born approximation for liquid sodium.

[39] D. Shoenberg and P. J. Stiles, Proc. Roy. Soc. (London) **A281**, 62 (1964); K. Akamura and I. M. Templeton, Phil. Mag. **8**, 889 (1963).

[40] R. Taylor, R. A. Moore, and S. H. Vosko, Can. J. Phys. **44**, 1995 (1966).

[41] J. J. Donaghy, A. T. Stewart, and D. M. Rockmore, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, 1965* (Plenum Press, Inc., New York, 1965), Part B, p. 835.

which is of little consequence to the present work but does suggest that symmetrized combinations of plane waves will be required to secure quantitative agreement with experiment.

The structure factor has already been discussed at some length in Sec. III. Truncation of the high-temperature expansion of $S'(\mathbf{q},\omega)$ after the first term may be questionable for lithium because of its high Debye temperature, but this poses no serious problem and we have made no estimates of the corrections. It is clear that one could easily take care of anharmonic contributions to the temperature dependence of the transport coefficients through that of the elastic constants.[42] Indeed, adequate structure factors seem to have become one of the least of our present worries, and it is obviously of interest to know to what extent the simple three-force-constant dynamical matrix could be trusted for other metals than the alkalis. Since completion of our calculations, it has come to our attention that a closely related model devised by Krebs[43] has been applied with appreciable success to Cu, Au,[44] and Ni,[45] as well as to the alkali metals.[43,46] (The Krebs model differs from ours primarily by including a Yukawa potential to represent long-range interionic interactions as screened by the electron gas.) For example, for Ni the phonon-dispersion curves determined by neutron scattering are quite well reproduced by a three-force-constant $D(\mathbf{q})$ fitted to the elastic constants. The simple parametrized dynamical matrix may prove to be rather widely applicable in problems in which it is only to be used as a calculational tool and the greatest accuracy is either not available (i.e., no neutron data exist) or not required. Of course a strong-coupling metal such as lead must be treated with considerable caution, if at all.

The only numerical approximation we have introduced is the replacement of Fermi surface averages by weighted symmetry point averages, and this of course would be exact if there were no anisotropy in the scattering.

The marked sensitivity of the computed transport coefficients to slight inaccuracies in the pseudopotential delineated in Sec. IV has of course been emphasized in regard to the resistivity by other workers.[21,47] The AHA potentials as computed, e.g., with band calculations in mind, were not really considered to have the greater accuracy required for the transport properties.[48] It is not likely that appreciably more precise pseudopotentials by direct computation will be available for some time. However, our results suggest that a phase-shift analysis such as that of Greene and Kohn[7] in which the scattering amplitude was adjusted to the diffusion thermopower as well as to the resistivity would produce an electron-ion pseudopotential of sufficient accuracy for most calculations. Roughly put, the resistivity probes the magnitude and the thermopower the shape of the pseudopotential.

The primary goal of this work has been attained: We have demonstrated that the positive diffusion thermopower of Li is a result of the unusual energy dependence of the electron-phonon interaction and have accounted for the extreme scattering anisotropy responsible for the anomalous effective carrier density in Li, and have shown that neither of these large effects requires any appreciable departure from the free-electron model. On the other hand, the diffusion thermopower of Cs is still not conclusively understood, and detailed exploration of the influence of the d bands would be particularly illuminating. We are finally led to expect that the positive thermopowers of Cu, Ag, and Au are also due primarily to Coulomb-core interference in the effective electron-ion interaction,[2] and anticipate that a calculation similar to that we have here presented would suffice to confirm this.

ACKNOWLEDGMENTS

We have profited from a number of useful conversations with G. Aldredge, S. Joshi, F. Mueller, and M. Rowe, from informative comments by M. H. Cohen, L. Falicov, and V. Heine; and we wish to thank P. Kendall for sending us his thermopower results in advance of their publication.

APPENDIX A

We adopt a rigid-ion model and take the scattering of an electron by the lattice ions to be through a superposition of local potentials[5,9]

$$U(\mathbf{r})=\sum_l V(\mathbf{r}-\mathbf{R}_l) \tag{A1}$$

$$=\frac{1}{N}\sum_{\mathbf{q}} V(\mathbf{q})\rho(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{A2}$$

Here

$$V(\mathbf{q})\equiv\frac{1}{\Omega_0}\int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}}V(\mathbf{r}), \tag{A3}$$

where N is the total number of ions, Ω_0 the ionic volume, $V(\mathbf{r})$ the interaction of an electron with one ion, and

$$\rho(\mathbf{q})=\int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}}\rho(\mathbf{r})=\sum_l e^{-i\mathbf{q}\cdot\mathbf{R}_l} \tag{A4}$$

is the Fourier space transform of the lattice number density, $\mathbf{R}_l$ being the position of the ion which in equilibrium is at the lattice point $\mathbf{l}$. Since we work in a pseudopotential scheme, we take simple plane waves

$$\langle\mathbf{r}|\mathbf{k}\rangle=(N\Omega_0)^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{r}) \tag{A5}$$

---

[42] See Ref. 7, but also Sec. II of Ref. 21.

[43] K. Krebs, Phys. Letters **10**, 12 (1964); Phys. Rev. **138**, A143 (1965).

[44] M. M. Shukla, Phys. Status Solidi **7**, K11 (1964); **8**, 475 (1965).

[45] S. Hautecler and W. Van Dingen, Physica **34**, 257 (1967).

[46] P. S. Mahesh and B. Dayal, Phys. Status Solidi **9**, 351 (1965).

[47] A. Meyer and W. H. Young, Phys. Rev. **139**, A401 (1965).

[48] V. Heine (private communication).

for the electrons and have

$$\langle \mathbf{k}' | e^{i\mathbf{q}\cdot\mathbf{r}} | \mathbf{k} \rangle = \delta_{\mathbf{k}',\mathbf{q}+\mathbf{k}}. \tag{A6}$$

(Note that $\mathbf{k}$ runs over the proper Brillouin zone while $\mathbf{q}$ can run over all values.) If we were to use symmetrized plane waves as basis functions, then the Kronecker symbol (A6) would be replaced by the product of a "lattice delta-function" enforcing conservation of crystal momentum and an additional matrix element. In the plane-wave representation then in the Born (or weak scattering) approximation the golden rule rate for the electronic transition $\mathbf{k} \to \mathbf{k}'$ is[20,49]

$$W_{\mathbf{k}',\mathbf{k}} = \frac{2\pi}{\hbar}\frac{1}{N}\sum_{\mathbf{q}} |V(q)|^2 \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}} \frac{1}{\hbar} S\left(\mathbf{q}, \frac{E_{\mathbf{k}'} - E_{\mathbf{k}}}{\hbar}\right), \tag{A7}$$

the Kronecker symbol being carried along in order to have the final summation we will need be on $\mathbf{q}$. We have written

$$S(\mathbf{q},\omega) = \frac{1}{2\pi}\int dt\, e^{-i\omega t} \frac{1}{N} \langle \rho(-\mathbf{q}, t)\rho(\mathbf{q},0)\rangle_T, \tag{A8}$$

where $\langle\ \rangle_T$ indicates the usual thermal trace and the density operators are in the Heisenberg picture. The normalization of $S(\mathbf{q},\omega)$ in (A8) corresponds to that of Greene and Kohn[7] and not, e.g., to that of van Hove.[20] Were we to use symmetrized plane waves, then instead of (A7) we would have a double sum, on $\mathbf{q}$ and $\mathbf{q}'$, say, and $S(\mathbf{q},\omega)$ would be supplanted by the Fourier time transform of $(1/N)\langle \rho(-\mathbf{q}', t)\rho(\mathbf{q},0)\rangle_T$. In constructing the collision term appropriate to a Boltzmann equation from $W_{\mathbf{k}',\mathbf{k}}$ and the rate $W_{\mathbf{k},\mathbf{k}'}$ for the inverse transition we make use of the condition of detailed balance[5,49,50] as expressed by

$$\begin{aligned}\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle \rho(-\mathbf{q}, t)\rho(\mathbf{q},0)\rangle_T \\ = e^{-\beta\hbar\omega}\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle \rho(\mathbf{q},0)\rho(-\mathbf{q}, t)\rangle_T,\end{aligned} \tag{A9}$$

where $\beta = 1/k_BT$, and obtain for the distribution function $f_{\mathbf{k}}$

$$\begin{aligned}\left[\frac{\partial f_{\mathbf{k}}}{\partial t}\right]_{\text{coll.}} &= \sum_{k'}\{W_{\mathbf{k},\mathbf{k}'}(1-f_{\mathbf{k}})f_{\mathbf{k}'} - W_{\mathbf{k}',\mathbf{k}}(1-f_{\mathbf{k}'})f_{\mathbf{k}}\} \\ &= \frac{2\pi}{\hbar}\frac{1}{N}\sum_{\mathbf{q}}|V(\mathbf{q})|^2\frac{1}{\hbar}S\left(\mathbf{q},\frac{1}{\hbar}[E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}]\right) \\ &\quad\times\{(1-f_{\mathbf{k}})f_{\mathbf{k}+\mathbf{q}}e^{\beta(E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}})} - (1-f_{\mathbf{k}+\mathbf{q}})f_{\mathbf{k}}\}.\end{aligned} \tag{A10}$$

Proceeding in standard fashion[5,50] we write

$$f_{\mathbf{k}} = f_{\mathbf{k}}^{(0)} - \Phi_{\mathbf{k}}\frac{\partial f_{\mathbf{k}}^{(0)}}{\partial E_{\mathbf{k}}}, \tag{A11}$$

where $f_{\mathbf{k}}^{(0)}$ is Fermi distribution function and, neglecting quantities of second order in Φ, find after some manipulation that the terms in curly brackets in (A10) reduce to

$$\{\ \} = \beta(1-f_{\mathbf{k}+\mathbf{q}}^{(0)})f_{\mathbf{k}}^{(0)}(\Phi_{\mathbf{k}+\mathbf{q}} - \Phi_{\mathbf{k}}). \tag{A12}$$

The Boltzmann equation in the presence of an effective electric field $\mathbf{F}$ is used to define a relaxation time $\tau(\mathbf{k})$ such that

$$\Phi_{\mathbf{k}} = (-e)\tau(\mathbf{k})\mathbf{F}\cdot\mathbf{v}_{\mathbf{k}}, \tag{A13}$$

$$\begin{aligned}\left[\frac{\partial f_{\mathbf{k}}}{\partial t}\right]_{\text{coll.}} &= -e\mathbf{F}\cdot\mathbf{v}(\mathbf{k})\frac{\partial f_{\mathbf{k}}^{(0)}}{\partial E_{\mathbf{k}}} \\ &= e\mathbf{F}\cdot\mathbf{v}(\mathbf{k})\beta(1-f_{\mathbf{k}}^{(0)})f_{\mathbf{k}}^{(0)},\end{aligned} \tag{A14}$$

where $\mathbf{v}(\mathbf{k})$ is the electronic group velocity. Inserting (A11)–(A14) into (A10) yields an integral equation for $\tau(\mathbf{k})$, namely,

$$\begin{aligned}&\mathbf{F}\cdot\mathbf{v}(\mathbf{k})(1-f_{\mathbf{k}}^{(0)}) \\ &= \frac{2\pi}{\hbar}\frac{1}{N}\sum_{\mathbf{q}}|V(\mathbf{q})|^2\frac{1}{\hbar}S\left(\mathbf{q},\frac{1}{\hbar}[E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}]\right)(1-f_{\mathbf{k}+\mathbf{q}}^{(0)}) \\ &\quad\times\{\tau(\mathbf{k})\mathbf{F}\cdot\mathbf{v}(\mathbf{k}) - \tau(\mathbf{k}+\mathbf{q})\mathbf{F}\cdot\mathbf{v}(\mathbf{k}+\mathbf{q})\}.\end{aligned} \tag{A15}$$

First we eliminate the electric field with the aid of cubic symmetry. Under any operation R of the point group, $V(\mathbf{q})$, $E(\mathbf{k})$, and $\tau(\mathbf{k})$ are invariant while $\mathbf{v}(R\mathbf{k}) = R\mathbf{v}(\mathbf{k})$ and $S(R\mathbf{q},\omega) = S(\mathbf{q},\omega)$. Multiply both sides of (A15) by $\mathbf{F}\cdot\mathbf{v}(\mathbf{k})$, replace $\mathbf{k}$ by $R\mathbf{k}$, and then average both sides over the operations of the group. The equation which results is

$$\begin{aligned}1 = &\frac{2\pi}{\hbar}\frac{1}{N}\sum_{\mathbf{q}}|V(\mathbf{q})|^2\frac{1}{\hbar}S\left(\mathbf{q},\frac{1}{\hbar}[E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}]\right)\frac{1-f_{\mathbf{k}+\mathbf{q}}^{(0)}}{1-f_{\mathbf{k}}^{(0)}} \\ &\times\left\{\tau(\mathbf{k}) - \frac{\mathbf{v}(\mathbf{k})\cdot\mathbf{v}(\mathbf{k}+\mathbf{q})}{v^2(\mathbf{k})}\tau(\mathbf{k}+\mathbf{q})\right\}.\end{aligned} \tag{A16}$$

We now separate the right-hand side of (A16) into two terms after adding and subtracting a term within the curly brackets.

$$\begin{aligned}1 = &\left\{\frac{2\pi}{\hbar}\frac{1}{N}\sum_{\mathbf{q}}|V(\mathbf{q})|^2\frac{1}{\hbar}S\left(\mathbf{q},\frac{1}{\hbar}[E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}]\right)\frac{1-f_{\mathbf{k}+\mathbf{q}}^{(0)}}{1-f_{\mathbf{k}}^{(0)}}\right. \\ &\left.\times\left(1-\frac{\mathbf{v}(\mathbf{k})\cdot\mathbf{v}(\mathbf{k}+\mathbf{q})}{v^2(\mathbf{k})}\right)\right\}\tau(\mathbf{k}) \\ &+\frac{2\pi}{\hbar}\frac{1}{N}\sum_{\mathbf{q}}|V(\mathbf{q})|^2\frac{1}{\hbar}S\left(\mathbf{q},\frac{E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}}{\hbar}\right)\frac{1-f_{\mathbf{k}+\mathbf{q}}^{(0)}}{1-f_{\mathbf{k}}^{(0)}} \\ &\times\frac{\mathbf{v}(\mathbf{k})\cdot\mathbf{v}(\mathbf{k}+\mathbf{q})}{v^2(\mathbf{k})}[\tau(\mathbf{k})-\tau(\mathbf{k}+\mathbf{q})].\end{aligned} \tag{A17}$$

A connection to more friendly territory than is represented by Eq. (A17) can be made by referring its right-

---

[49] A. Sjölander, in *Phonons and Phonon Interactions*, edited by T. Bak (W. A. Benjamin, Inc., New York, 1964).

[50] Reference 17, Chaps. 8, 9.

hand side to conditions under which the scattering is elastic and τ is a function of electronic energy only. In that case, the second term vanishes identically and the first yields up for $\tau(\mathbf{k})$ the golden rule time for the relaxation of the particle current in the direction $\hat{k}$. In the general case, the summand of the second term has a number of zeros not shared by that of the first term. It vanishes for any $\mathbf{q}$ giving scattering at 90°. Every vector $R\mathbf{k}$ of the star of $\mathbf{k}$ occurs among the $\mathbf{k}+\mathbf{q}$ in the sum on $\mathbf{q}$ and at each such $\mathbf{q}$ we have $\tau(\mathbf{k})-\tau(\mathbf{k}+\mathbf{q})$ going through zero by symmetry. Since under cubic symmetry there are 48 such zeros for a general $\mathbf{k}$, each such scattering event being elastic, there are wholesale cancellations. In marked contrast, the summand of the first term could vanish only exceptionally, for example, for small angle scattering which either is inelastic or is on a substantially anisotropic energy surface. For elastic scattering and isotropic $E(\mathbf{k})$, the summand of the first term is always positive, while that of the second retains all the zeros just mentioned. Accordingly, we expect to obtain a reasonable approximation to $\tau(\mathbf{k})$ by retaining only the first term on the right-hand side of Eq. (A17).

Concentrating now on high temperatures, we may take the scattering to be elastic insofar as the electrons are concerned,[7] and write

$$(1/\hbar)S\{\mathbf{q},(1/\hbar)[E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}]\}=\delta(E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}})S(\mathbf{q})\,,\quad\text{(A18)}$$

where $S(\mathbf{q})$ is the static-structure factor.[51] We now specialize to isotropic energy $E(\mathbf{k})=E(k)$, and also take V to be spherically symmetric. Retaining only the main term of Eq. (A17) we find

$$\tau^{-1}(\mathbf{k})=\left(\frac{2\pi}{\hbar}\right)N^{-1}\sum_{\mathbf{q}}|V(q)|^2\left(\frac{-\mathbf{q}\cdot\mathbf{k}}{k^2}\right)S(\mathbf{q})\times\delta[E(\mathbf{k}+\mathbf{q})-E(\mathbf{k})].\quad\text{(A19)}$$

Converting the sum to an integral, assuming $E(k)$ parabolic with effective mass m^*, and introducing the mean free path

$$l(\mathbf{k})=v(\mathbf{k})\tau(\mathbf{k})\,,\quad\text{(A20)}$$

we obtain finally

$$\left[\frac{1}{l(\mathbf{k})}\right]=\left(\frac{\Omega_0}{4\pi}\right)\left(\frac{m^{*2}}{\hbar^4k^4}\right)\int_0^{2k}dq\,q^3|V(q)|^2S(\hat{k},q)\,,\quad\text{(A21)}$$

where

$$S(\hat{k},q)=(1/2\pi)\int d\Omega(\hat{q})S'(\mathbf{q})\delta\left[\hat{q}\cdot\hat{k}+\left(\frac{q}{2k}\right)\right].\quad\text{(A22)}$$

We have put a prime on the structure factor to emphasize that the Bragg peaks associated with the static lattice are to be omitted since they have been included in the crystal potential and their effects are supposed to be contained in the electronic basis functions.

If the scattering potential is taken to be a single lattice sum of nonlocal operators, then the only change from (A7) through (A19) is to replace $V(\mathbf{q})$ by $V_{\mathbf{k}}(\mathbf{q})=N\langle\mathbf{k}+\mathbf{q}|V|\mathbf{k}\rangle$. Eq. (A21) is recovered since for any single-ion pseudopotential $V_{\mathbf{k}}(\mathbf{q})$ is axially symmetric about $\mathbf{k}$.

We could, of course, define in obvious fashion a sequence of successive approximations or a perturbation expansion to improve upon Eq. (A19). However, the labor required to compute even the second approximation is considerably greater than is warranted in view of the inaccuracies of presently available pseudopotentials, and seems unlikely to result in changes of more than a few percent.

APPENDIX B

Using a Born–von Kármán model for a body-centered cubic lattice, Squires[27] has expressed the dynamical matrix in terms of the matrix of force constants $[\phi_{ij}{}^s]$:

$$D_{i,i}=\sum_s\frac{n_s}{6M}\sum_j\phi_{jj}{}^s\{2-C_{j,i}{}^s[C_{j+1,i+1}{}^sC_{j+2,i+2}{}^s+C_{j+2,i+1}{}^sC_{j+1,i+2}{}^s]\}\,,$$

$$D_{i,i+1}=\sum_s\frac{n_s}{6M}\sum_j\phi_{j+1,j+2}{}^sC_{j,i+2}{}^s[S_{j+1,i}{}^sS_{j+2,i+1}{}^s+S_{j+2,i}{}^sS_{j+1,i+1}{}^s].$$

Here i and j label the Cartesian co-ordinates and s labels the neighbor shell. The spatial variation of the normal modes is taken to be $\exp[i\mathbf{q}\cdot\mathbf{R}_{\mathrm{n}}]$; the C's and S's are defined by

$$C_{ji}{}^s=\cos\tfrac{1}{2}ah_j{}^sqi,\quad S_{j,i}{}^s=\sin\tfrac{1}{2}ah_j{}^sqi\,,$$

and the values of $h_j{}^s$, n_s, and s as follows:

s	$h_1{}^s$,	$h_2{}^s$,	$h_3{}^s$	n_s
1	1	1	1	8
2	2	0	0	6
3	2	2	0	12
4	3	1	1	24
5	2	2	2	8

Squires has also obtained the following expressions for the elastic constants:

$$C_{11}=\sum_s\frac{n_s}{12a}\sum_j(h_j{}^s)^2\phi_{jj}{}^s\,,$$

$$C_{44}=\sum_s\frac{n_s}{24a}\sum_j[(h_{j+1}{}^s)^2+(h_{j+2})^2]\phi_{jj}{}^s\,,$$

$$C_{12}+C_{44}=\sum_s\frac{n_s}{6a}\sum_j h_{j+1}{}^sh_{j+2}{}^s\phi_{j+1,j+2}{}^s.$$

---

[51] See, e.g., the Appendix of Ref. 7.