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Thermoelectric Power in the Nearly-Free-Electron Model*

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The thermoelectric power in the nearly-free-electron model is re-examined with specific reference to the especially long-standing theoretical problem posed by occurrences among pure monovalent metals of a negative Hall coefficient but a positive electron-diffusion thermopower. The physical picture is clarified by referring steady-state excitations of the electron gas to the current-free equilibrium distribution, and a summary is given of the evidence which shows Fermi-surface anisotropy to be unimportant for an explanation of the "reversed sign" thermopowers. It is pointed out that the scattering of an electron by the pseudopotential of a single ion generally exhibits Coulomb-core interference which is the analog of the Coulomb-nuclear interference in nuclear physics, and that this can yield the required energy dependence of the transport mean free path. This is illustrated by a model calculation which allows analytic evaluation of all results and which contains only the simplest ingredients: free electrons, a relaxation time, an isotropic elastic-continuum structure factor for acoustic phonons, and a point-ion pseudopotential. The model can accommodate a rather wide range of thermopower coefficients of either sign, and allows a sharp reversal of sign for modest changes of the parameters. Although no quantitative comparison is attempted, estimates of the parameter values appropriate to real systems indicate that Coulomb-core interference effects discriminate between real metals rather satisfactorily and are, in fact, strong enough to produce positive thermopowers with little, if any, additional help.

I. INTRODUCTION

FOR more than thirty years the absolute thermoelectric power of pure samples of monovalent metals (at STP) has remained a nagging embarrassment to the theory of the ordinary electronic transport properties of solids.[1–10] All familiar simple theory has promised us that in these materials the sign of the electron-diffusion contribution to the thermopower should be that of the charge carriers as determined by the Hall effect, i.e., negative; but instead it turns out to be positive for Cu, Ag, Au, and—even more perversely—for Li alone of the solid alkalies. At least two generations of experimentalists have remained completely unshaken in testifying to these results as obstinate facts of life, and considerable effort has been expended unsuccessfully to explain them. Accordingly, it is of interest to display in this paper a very simple model calculation which relies on general features of the electron-phonon interaction which have become well established only in relatively recent times, and which for physically reasonable parameter values can yield either a positive or a negative thermopower.[11]

It is generally agreed among thermoelectricians that in solid noble metals the origin of the positive sign must in large part lie in the energy dependence of the electronic mean free path.[12,13] The viewpoint underlying this paper goes rather further and is: The *primary* ingredients in understanding the high-temperature thermopower of *all* the monovalents can be fitted into a nearly-free-electron model, provided that the effective electron-ion interaction is treated reasonably well. This position is, seemingly, diametrically opposed to that of previous theoretical attempts, all of which have relied heavily upon departures of the real world from free-electron models. In Sec. II the physical situation at a microscopic level is examined and such of the accumulated theoretical experience and experimental evidence as bears most directly on the present standpoint is summarized.

In Sec. III we show that the form of both the electron-ion pseudopotential in simple metals and of the corresponding screened deformation potential in degenerate semiconductors can lead to a mean free path rapidly decreasing with increasing energy and hence to a "reversed" sign in the electron-diffusion thermopower. To illustrate this we adopt in Sec. IV a simplified model interaction and evaluate analytically the high-temperature mean free path and thermopower for free electrons, and give plots of the latter as a function of the parameters.

The applicability and significance of these results to real systems is discussed in the last section. Since for the sake of simplicity the model calculation uses an

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[1] No attempt is made here to review the evolution of the present state of knowledge of thermoelectric power in monovalent metals. The following references may be consulted for discussions of the experimental data and various aspects of the theory at different stages of their development.

[2] G. Borelius, Proc. Roy. Acad. Amsterdam **33**, 17 (1930).

[3] A. Sommerfeld and N. H. Frank, Rev. Mod. Phys. **3**, 1 (1931).

[4] D. K. C. MacDonald, *Thermoelectricity: An Introduction to the Principles* (John Wiley & Sons, Inc., New York, 1962).

[5] J. S. Dugdale, Science **134**, 77 (1961).

[6] N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958).

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

[8] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Sec. 33.

[9] F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4.

[10] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1962).

[11] A preliminary account was given by J. E. Robinson [Bull. Am. Phys. Soc. **10**, 325 (1965)].

[12] J. M. Ziman, Advan. Phys. **10**, 1 (1961).

[13] F. J. Blatt, Phys. Letters **8**, 235 (1964).

isotropic Debye structure factor[14] for the phonons, quantitative comparison to experiment is not attempted. Nevertheless, the indications for the monovalents suggest that their thermopowers could be accounted for at least semiquantitatively with little if any help from Fermi-surface distortion if accurate electron-ion interactions and structure factors were in hand.

II. THE PHYSICAL PICTURE

A positive thermopower in a gas of free electrons would seem to present a conceptual difficulty to many physicists, since it implies that under the influence of a temperature difference the *diffusive* motion of the carriers is upward *against* the temperature gradient. It is hence more than ordinarily helpful to develop a physical picture, and to this end it is advantageous to examine in some detail the solution of the relevant Boltzmann equation when a relaxation time $\tau(\mathbf{k})$ exists. The nature of the electron steady-state distribution function $f(\mathbf{k})$ in the presence of a thermal gradient ∇T is quite clearly described by Ziman,[15] but we need here to carry the discussion a step further. We write

$$f_1(\mathbf{k})\equiv f(\mathbf{k})-f_0(\mathbf{k})=\{-\partial f_0/\partial\epsilon(\mathbf{k})\}\{[\epsilon(\mathbf{k})-\zeta](1/T)\times(-\nabla T)\cdot\mathbf{l}(\mathbf{k})+(-e\mathbf{E})\cdot\mathbf{l}(\mathbf{k})\}, \quad (2.1)$$

$$\mathbf{l}(\mathbf{k})=\tau(\mathbf{k})\mathbf{v}(\mathbf{k}), \quad (2.2)$$

$$j_1(\mathbf{k})=[-e\mathbf{v}(\mathbf{k})]f_1(\mathbf{k}). \quad (2.3)$$

Here, $f_0(\mathbf{k})$ is the Fermi function, $\epsilon(\mathbf{k})$ and $\mathbf{v}(\mathbf{k})$ are the electron energy and group velocity, ζ the chemical potential, $(-e)$ the electron charge, and $\mathbf{E}$ the effective electric field. Discarding the "background" $f_0(\mathbf{k})$, the microscopic contribution to the current arising from carriers near $\mathbf{k}$ is

$$2(2\pi)^{-3}d^3k\, j_1(\mathbf{k})=2(2\pi)^{-3}d\epsilon[dA(\epsilon,\hat{k})/\hbar v(\mathbf{k})]j_1(\mathbf{k}) = (-e/4\pi^3\hbar)d\epsilon\, dA(\epsilon,\hat{k})f_1(\mathbf{k})\hat{v}(\mathbf{k}), \quad (2.4)$$

where $dA(\epsilon,\hat{k})$ is that energy surface area element which subtends the solid angle $d^2\hat{k}$ about the direction $\hat{k}$. Note that these expressions are quite general within the context of Boltzmann equation plus relaxation time. The quantity in braces { } in (2.1) is the work done *on* a carrier during one collision-free flight, and a key fact is that the entropy of transfer $\{[\epsilon(\mathbf{k})-\zeta]/T\}$ and hence the effective "thermal force" on a carrier changes sign at the Fermi level ζ.[16] The direction of the net diffusion is thus determined by competition between carriers below and carriers above the Fermi level in which those with the greater free path tend to win, and nothing in the structure of (2.1)–(2.4) forces that direction to be *down* the temperature gradient. It is interesting to note in this connection that the theory of the spectacular fountain effect and thermal conductivity in liquid He II was initially stimulated by that of thermoelectricity.[17]

It is particularly vivid to describe $f(\mathbf{k})$ in terms of particles and holes referred to $f_0(\mathbf{k})$, the current-free equilibrium distribution at finite temperature. Since $f_1(\mathbf{k})$ is exactly antisymmetric about $\mathbf{k}=0$ by virtue of the time reversal symmetry of $\epsilon(\mathbf{k})$ and $\tau(\mathbf{k})$, $f(\mathbf{k})$ is exactly that distribution which would be produced by transferring electrons from $\mathbf{k}$ to $-\mathbf{k}$, i.e., by creating particles (charge $-e$) in $-\mathbf{k}$ and holes (charge $+e$) in $\mathbf{k}$. This is illustrated in Fig. 1. There is here, of course, no direct relation to the electronlike or holelike characteristics of an underlying band structure. For example, the only explicit emergence of the band structure in (2.4) is, through $dA(\epsilon,\hat{k})$, in determining the amount of phase space at given energy available for creation of excitations from equilibrium. Because of the exact symmetry of $\mathbf{j}_1(\mathbf{k})$ about $\mathbf{k}=0$ and of the $(-\partial f_0/\partial\epsilon)$ factor, we can confine our attention to the vicinity of the Fermi level and to particles and holes moving down the gradient. We need discuss only that electrical current which would be produced by $(-\nabla T)$ acting alone, taking $\mathbf{E}$ to be whatever is necessary for its complete cancellation.

The qualitative behavior of $f_1(\mathbf{k})$ near the Fermi level is determined by the energy dependence of $l(\epsilon,\hat{k})$; the three cases which can arise are schematized in Fig. 2. When the mean free path is independent of energy, $f_1(\mathbf{k})$ exhibits exact particle-hole symmetry about the Fermi level for every $\hat{k}$. If $dA(\epsilon,\hat{k})$ were symmetric about ζ, then the current due to $(-\nabla T)$ would vanish *micro*scopically and *a fortiori* the thermopower would be

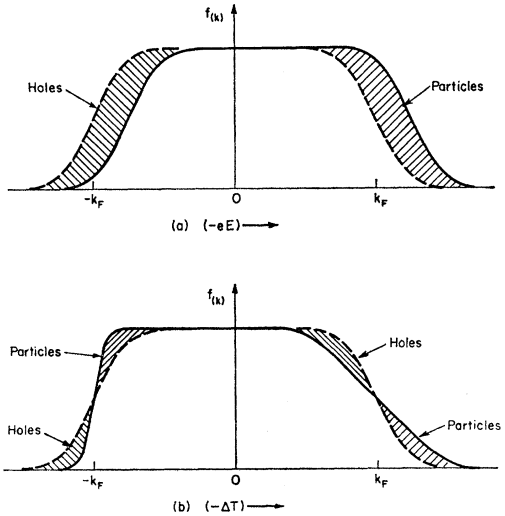

FIG. 1. Particle-hole structure of the steady-state distribution function. Solid lines: steady-state distribution $f(\mathbf{k})$, dashed lines: equilibrium distribution $f_0(\mathbf{k})$. (a) Electric field acting alone, directed as indicated. (b) Temperature gradient acting alone, directed as indicated.

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[14] This terminology is defined in Sec. IV.

[15] Reference 10, Secs. 9.9 and 9.10.

[16] See, e.g., S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1952), Chap. III.

[17] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1954), Vol. II, p. 73.

zero. For the moment, let us stick with $dA(\epsilon,\hat{k})$ increasing at ζ, i.e., to an electronlike Fermi surface. Since the phase space for creating excitations at given $|\epsilon(\mathbf{k})-\zeta|$ is greater for particles than for holes, the net electron current is down the temperature gradient and the thermopower is negative. When $[\partial l(\mathbf{k})/\partial\epsilon]_{\zeta=\epsilon}>0$, $f_1(\mathbf{k})$ itself is unbalanced in favor of particles and the thermopower will be more strongly negative. When, however, $[\partial l(\mathbf{k})/\partial\epsilon]_{\epsilon=\zeta}<0$, then $f_1(\mathbf{k})$ contains more holes than particles and if the excess is sufficiently pronounced to overcome the phase-space asymmetry, the net electron flow will be *up* the temperature gradient and the thermopower will be *positive*. The corresponding statements for holelike $dA(\epsilon,\hat{k})$ are obvious. To translate all this into mathematics we would, for fixed $\hat{k}$ in (2.1)–(2.4), expand everything in sight but $(-\partial f/{}_0\partial\epsilon)$ in Taylor series in $\epsilon=\epsilon(\mathbf{k})-\zeta$. Integration of (2.4) over ϵ would then give a microscopic or partial thermopower, depending in general on $\hat{k}$. This might be done to advantage when, for example, the Fermi surface has both electronlike and holelike directions. The full thermopower is then obtained from the average over the Fermi surface of the partial thermopower weighted by $l(\zeta,\hat{k})$ just as for a many-band model.[18]

It can now be concluded that the sign of the diffusion thermopower is always that of the carriers which dominate the flow down the temperature gradient provided that the carriers are taken—as they should be taken—to be the particles and holes required to excite the system from equilibrium to steady state. We have no right to complain if this sign differs from that of the low-field isothermal Hall coefficient, since the steady-state excitation structure is qualitatively different for the two effects: In the Hall effect, along a given direction $\hat{k}$ we find either particles or holes but not both.

All previous attacks on the positive thermopower problem have relied either exclusively or in an essential way on nonspherical distortion of the Fermi surface, i.e., on the influence of the phase space.[19] However, as emphasized by Ziman, a Fermi surface sufficiently holelike to give unaided a sizeable positive thermopower would also lead to a positive Hall coefficient.[12] In retrospect it is a comfort that Ham's calculations[20] for the alkalies and Ziman's[12] for the noble metals showed Fermi-surface distortion alone to be inadequate to the need. The possibility that "simple" anisotropy of $\tau(\mathbf{k})$ might turn the trick was shown by Taylor's detailed calculation[21] to be another false hope. The candidacy of electron-electron scattering advanced by Blatt[13] has not been fully tested, but rests specifically on the holelike curvature in the necks of noble-metal Fermi surfaces.

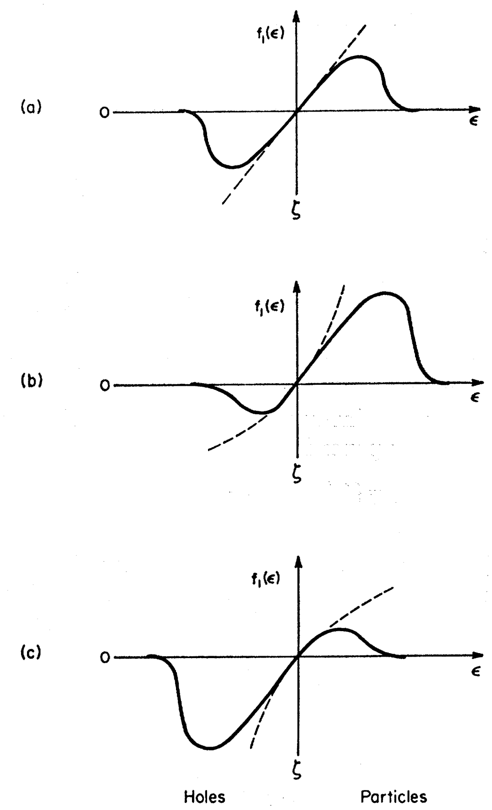

FIG. 2. Determination of the deviation from the equilibrium distribution by the mean-free-path energy dependence. Schematization for carriers moving down a temperature gradient acting alone. Dashed lines: $(\epsilon-\zeta)l(\epsilon)$. Solid lines: $f_1(\epsilon)=(-\partial f_0/\partial\epsilon)(\epsilon-\zeta)\times l(\epsilon)(1/T)|-\nabla T|$. (a) $l=$constant, (b) $(\partial l/\partial\epsilon)_\zeta>0$, (c) $(\partial l/\partial\epsilon)_\zeta<0$.

In fact, there are several indications that Fermi-surface anisotropy cannot be essential. First of all, thermopowers of Li, Cu, Ag, and Au remain positive in the liquid state.[22] Secondly, the Ettingshausen and Ettingshausen–Nernst coefficients are, where they are known, negative for these metals,[23,24] and indicate a dominance of excitation holes. Thirdly, the calculations of Sjundstrom[25] give the correct (i.e., positive) sign for liquid Li (see Sec. V). Accordingly, not only are we forced to seek the resolution of the problem in a strongly negative $[\partial l(\mathbf{k})/\partial\epsilon]_\zeta$ but are guaranteed that such exists and can be obtained for a spherical Fermi surface. The key, of course, is to find a scattering model which can yield such a mean free path, and to this task we now turn.

III. MODEL PSEUDOPOTENTIAL

We have now to produce in the scattering of free electrons by the thermal vibrations of the lattice ions a

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[18] Reference 7, Sec. 8.42.

[19] See, e.g., Ref. 6, p. 312; Ref. 7, p. 207; Ref. 10, p. 399. See also I. V. Abarenkov and M. V. Vedernikov, Fiz. Tverd. Tela **8**, 236 (1966) English transl.: Soviet Phys.—Solid State **8**, 186 (1966)].

[20] F. S. Ham, Phys. Rev. **128**, 82 (1962); **128**, 2524 (1962).

[21] P. L. Taylor, Proc. Roy. Soc. (London) **A275**, 209 (1963).

[22] N. E. Cusack, *Reports on Progress in Physics* (The Institute of Physics and The Physical Society, London, 1963), Vol. 26, p. 361.

[23] Reference 7, Secs. 8.532 and 8.54.

[24] J. -P. Jan, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. V, pp. 64–66.

[25] L. J. Sjündstrom, Phil. Mag. **11**, 657 (1965).

mechanism which can lead to a mean free path such that $[\partial l(\epsilon)/\partial\epsilon]_\zeta < 0$. In all electron-phonon models the Golden Rule rate for the transition $\mathbf{k} \rightarrow \mathbf{k}+\mathbf{q}$ can be taken proportional to a phonon structure factor $S(\mathbf{q})$ and to the absolute square of a form factor or coupling function $V(\mathbf{q})$. As Ziman has stressed,[26] if the maximum $|\mathbf{q}|$ for elastic scattering (i.e., $2k_F$) is close enough to the shortest reciprocal lattice vector, and provided that $V(2k_F)$ is large enough, then the rapid rise of $S(\mathbf{q})$ to its first maximum can turn the trick. However, although this Bragg peak rise in $S(\mathbf{q})$ is certainly essential to quantitative calculation, it is by itself neither necessary nor sufficient to obtain a positive thermopower, and we now concentrate on $V(\mathbf{q})$.

A simple model interaction which exhibits all features essential to this paper is

$$V(q) = \{1/\kappa(q)\}\{D - (4\pi N e^2/q^2)\}, \tag{3.1}$$

where D is a constant, N is the mean carrier density, and $\kappa(q)$ is the static dielectric function due to the carriers. In a deformation potential treatment, D is the "bare" deformation potential and the bare Coulomb term arises from the charge shifted to keep the chemical potential constant.[27] In a rigid-ion model this is exactly the "point-ion" interaction used extensively by Harrison[28] as a semiquantitative approximation to the electron-ion pseudopotential in simple metals. The bare electron-ion interaction is just the long-range Coulomb term due to the ionic charge $Ze = (N\Omega_0 e)$ together with a δ function of strength D to approximate the short-range terms (including orthogonality repulsion). Dielectric screening of the bare interaction is of course necessary in either model and ensures the proper limit $V(0) = -\frac{2}{3}E_F$. Equation (3.1) is both the simplest physically reasonable form for $V(q)$ and, with appropriate interpretation, applicable rather widely. Of course, one must not use (3.1) when very large q are required, since it remains finite for $q \rightarrow \infty$. This is of no practical concern here since we are dealing with the scattering of plane-wave electrons and hence with q no greater than about $2k_F$.

The characteristic of the model $V(q)$ which is central to this discussion is that it can vanish at finite q. If it does, every scattering cross section (differential, total, momentum transfer) will exhibit a minimum as a function of energy, and on the high-energy side of the minimum we shall have $dl(\epsilon)/d\epsilon < 0$. Such a maximum in $l(\epsilon)$, if it is sharp enough and lies somewhat below the Fermi level, obviously produces a "reversed sign" in the thermopower. Indeed, because large momentum transfers are preferentially weighted in $l(\epsilon)$, a positive thermopower can result even if $V(q)$ does not actually go through zero.

This behavior should not be confused either with a Ramsauer-Townsend effect or with a resonance or antiresonance. We have here the solid-state counterpart of the long familiar interference between Coulomb and nuclear scattering in low-energy nuclear physics. In the nuclear case, interference can lead to a reduction in total cross section over a narrow interval of incident energy[29] by as much as two orders of magnitude. We mention this not to imply anything quantitative for the solid-state case, but to nullify any predisposition to regard such Coulomb-core interference effects, associated with a single ion, as being necessarily small.

We close this section by indicating the adaption of $V(q)$ to a degenerate semiconductor case. First the bare Coulomb charge-shift term becomes $(4\pi N e^2/\kappa_0 q^2)$, where κ_0 is the static dielectric constant of the host material. We take the polarizabilities of the host and of the free carriers to be additive and interpret $\kappa(\mathbf{q})$ in Eq. (3.1) as $1 + 4\pi\alpha(\mathbf{q})/\kappa_0$, where $\alpha(\mathbf{q})$ is the total polarizability due to the free carriers. This interpretation of $\kappa(\mathbf{q})$ is necessary if D is to represent an ordinary deformation potential in the limit of vanishing carrier concentration. Formal complications, e.g., associated with many-valley aspects, arise primarily in trying to use $V(\mathbf{q})$ in a calculation, not in its form.

IV. NUMERICAL MODEL CALCULATION

The primary effects of Coulomb-core interference on the mean free path and thermopower can be displayed adequately within the simplest possible theoretical framework. We assume a free-electron energy spectrum $\epsilon_k \sim k^2$, a Bravais lattice, complete isotropy for the phonons, a Boltzmann equation, and take the temperature to be high enough to obviate any difficulty in defining a relaxation time. The electron diffusion thermopower is then given by

$$S_e = \frac{k_B^2 T}{3(-e)\zeta}\left\{1 + \left(\frac{\epsilon}{l}\frac{dl}{d\epsilon}\right)_\zeta\right\}$$
$$\equiv \frac{kB^2T}{3(-e)\zeta}\xi. \tag{4.1}$$

The scattering may be taken to be elastic insofar as the electrons are concerned, and in the Born, or "weak scattering,"[30] approximation we have[31]

$$\frac{1}{l_k} = \frac{(m^*)^2}{\pi\hbar^4}\frac{4}{(2k)^4}\int_0^{2k} dq\, q^3 |V(q)|^2 \Omega S(q), \tag{4.2}$$

where m^* is the effective electronic mass, Ω is the normalization volume, and $S(q)$ the static structure

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[26] J. M. Ziman, Phil. Mag. **6**, 1013 (1961).

[27] Reference 10, Sec. 5.6.

[28] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966), Sec. 2.9.

[29] J. E. Brolley, Jr., J. D. Seagrave, and J. G. Beery, Phys. Rev. **135**, B1119 (1964).

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

[31] Equation (4.2) can be derived in the simplest form of Bloch-Wilson theory; no variational theorem is involved. See e.g., Ref. 28, p. 133.

factor.[32] Note particularly that Eq. (4.2) holds for any k. It is worth emphasizing that the limits on integration over momentum transfer $\hbar\mathbf{q}$ are for elastic scattering *always* determined, for any ϵ, by the electron energy surface, since this fact tends to get lost in a labyrinth of umklapp complications in treatments which do not explicitly collect all the lattice dynamics into a structure factor. Under our assumption of high temperature, $S(q)$ is proportional to T.

We now approximate $S(q)$ by its elastic continuum limit $S(0)$. This is just a slightly disguised and different version of the simplest Debye model, and we shall use the name (isotropic) Debye structure factor to refer to it. We hereby amputate the Bragg peak rises from $S(q)$, and have for $T>\Theta_D$

$$\Omega S(q)\rightarrow(k_BT/\rho_{\text{ion}}c_l^2)\,, \tag{4.3}$$

where ρ_{ion} is the mass density of the ion lattice and c_l the velocity of longitudinal acoustic waves. In perhaps more familiar terms we are treating umklapps like normal processes and hence neglect transverse waves completely.[33] By making this rather drastic approximation we place all responsibility for energy dependence of the mean free path squarely on the pseudopotential. In addition, for $\kappa(q)$ we use the Fermi-Thomas dielectric function

$$\kappa(q)\rightarrow 1+(k_s^2/q^2)\,, \tag{4.4}$$

where k_s is the usual screening constant. Neither of these approximations is essential, but they allow elementary analytic evaluation of everything.

It is convenient to measure the mean free path by a constant l_0 defined by

$$\frac{1}{l_0}=\frac{(m^*)^2D^2k_BT}{\pi\hbar\rho_{\text{ion}}c_l^2}. \tag{4.5}$$

Taking the mean free path to be l_0 would correspond to the venerable approximation of $V(q)$ by a constant, although D is not the same as the old interaction constant C. We also define two parameters

$$x\equiv(k_s^2/4k_F^2)\,, \tag{4.6}$$

$$A\equiv(|V(0)|/D)\,. \tag{4.7}$$

Equations (4.2)–(4.7) and the familiar $|V(0)|=(4\pi Ne^2/k_s^2)$ then give

$$\frac{l_0}{l(\epsilon_k)}=\frac{4}{(2k)^4}\int_0^{2k}dq\,q^3\left\{\frac{1-A(k_s^2/q^2)}{1+(k_s^2/q^2)}\right\}^2. \tag{4.8}$$

Elementary integration then yields

$$\frac{l_0}{l(\zeta)}=R(x,A)\,, \tag{4.9}$$

$$\left(\frac{d\ln l}{d\ln\epsilon}\right)_\zeta=2-\frac{2}{R(x,A)}\left(\frac{1-Ax}{1+x}\right)^2, \tag{4.10}$$

where

$$R(x,A)\equiv 1+2(A+1)^2\frac{x}{1+x}-2(A+1)(A+3)\left\{x-x^2\ln\left(1+\frac{1}{x}\right)\right\}. \tag{4.11}$$

Equations (4.9)–(4.11) constitute our principal formal results and show considerable variation in behavior as functions of A and x. Note that according to Eqs. (4.10) and (4.1) the thermopower coefficient ζ is never greater than three, which would be the value found for $N\geqslant\frac{1}{4}$ per atom if a Debye *cutoff* on the q integration were used[34] and umklapprozesse were discarded completely. If we fix the carrier density (i.e., take $x=$ constant) and increase D from a small positive value this maximum is reached just when the zero of the model pseudopotential passes $2k_F$ into the range of elastic momentum transfers.

When the Fermi surface consists of a number of separated spherical pieces, these expressions can be used to describe the intravalley scattering within one of the pieces, provided A and x are properly related to the number and structure of the valleys. For illustrative purposes we stick to a (simply connected) free-electron Fermi surface. In this case

$$x=(1/\pi a_Bk_F)=0.166r_s\,, \tag{4.12}$$

where a_B is the effective Bohr radius $(\hbar/m^*e^2)$ and r_s the usual dimensionless radius of the volume per carrier. We further write

$$x_0=(1/\pi a_Bk_0)\operatorname{sgn}D\,, \tag{4.13}$$

where

$$k_0^2\equiv(2m^*|D|/\hbar^2)\,, \tag{4.14}$$

and display in Figs. 3 and 4 numerical plots of Eq. (4.10) as functions of x, x_0. It is quite clear from these curves that a wide range of thermopower coefficients can be accommodated within the free-electron model. The sharp sign reversals for $x_0>0$ result from the onset of strong Coulomb-core interference. Note that $\xi<0$ can obtain for low density (large x), the point being that for a small Fermi surface only normal process scattering can occur. Accordingly we see that free electrons in a band of standard form, for which the Hall coefficient is always negative, can exhibit a positive diffusion thermopower entirely as a result of Coulomb-core interference, without any influence whatsoever either of

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[32] $S(q)$ is the Fourier space transform of the density-density correlation function of the lattice at finite temperature. Sometimes, perhaps confusingly, the term structure factor is used to designate a rather different quantity (see, e.g., Ref. 28, Sec. 2.5).

[33] See, e.g., J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964), Sec. 6.2.

[34] Reference 7, Secs. 9.34 and 8.42.

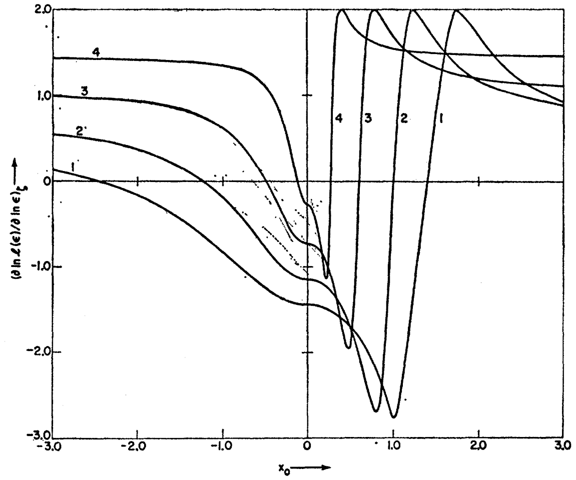

FIG. 3. Variation of $(\partial \ln l/\partial \ln \epsilon)_\zeta$ with strength of core δ function at fixed charge density. (1) $x=2.0$, $r_s=12.1$; (2) $x=1.0$, $r_s=6.0$; (3) $x=0.4$, $r_s=2.4$; (4) $x=0.1$, $r_s=0.6$. See text for parameter definitions.

anisotropy or of umklapprozesse. Corresponding statements for "free holes" in an inverted band of standard form are obvious.

An innocent expectation based solely on charge density considerations might be that a number of semimetals and degenerate semiconductors would have reversed sign thermopowers. Indeed, arsenic does show a positive Hall coefficient together with a negative thermopower.[35] However, this model calculation has little direct relevance for such materials. In semiconductors, the presence of ionized donors or acceptors and (in compound semiconductors) of polar optical modes invalidates the scattering model. In semimetals, the Fermi surface is generally too sensitively complicated for a free electron ϵ_k to have much meaning. Therefore, we turn now to monovalent metals.

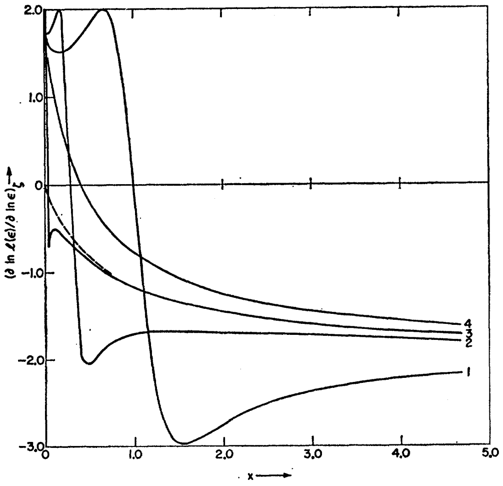

FIG. 4. Variation of $(\partial \ln l/\partial \ln \epsilon)_\zeta$ with charge density at fixed strength of core δ function. (1) $x_0=1.0$, (2) $x_0=0.5$, (3) $x_0=0.1$, (4) $x_0=0.5$. For an effective mass equal to the electron mass these corresponds to (1) $D=0.10$ Ry, (2) $D=0.41$ Ry, (3) $D=10.1$ Ry. See text for parameter definitions. The dashed line is for $x_0=0$.

V. SOLID MONOVALENT METALS

Exploration of the pertinence of the arguments and formal results of the last two sections to real systems commences with the alkali metals. Firstly, their Fermi surfaces may reasonably be taken approximately spherical, and secondly, they are simple metals. (A simple metal is here to be understood as one for which a small core approximation[36] is meaningful, or in particular any of the 25 elements for which Animalu and Heine have calculated pseudopotentials.[37]) Relevant values of the parameter x_0 for the alkalies can be estimated by fitting Eq. (3.1) to the Animalu-Heine-Abarenkov (AHA) pseudopotentials. Since we can choose to make the fit in a few ways, e.g., at the first zero of the AHA potentials or at $2k_F$, we do not determine a unique value but a range of x_0.

The well-known Fermi-surface anisotropy[12] in the solid noble metals could hardly be preserved in the liquid state, and hence, as remarked at the end of Sec. II, we regard a spherical Fermi surface for them, too, as adequate to the present purpose. Moreover, it has been shown by Mueller[38] and by Heine[39] that for Cu an effective interaction can be defined for an electron near

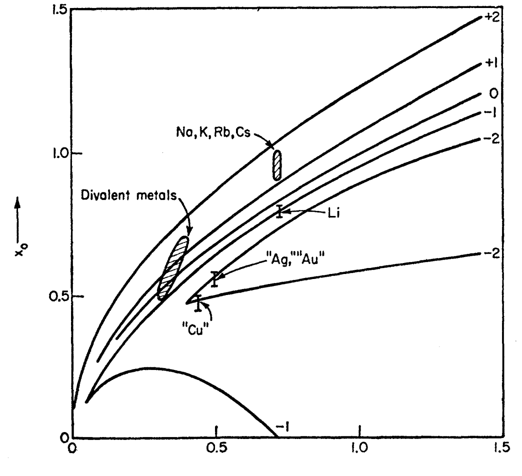

FIG. 5. Indications for real metals of the free-electron-model calculation. Contours of constant $[\partial \ln l(\epsilon)/\partial \ln \epsilon]_\zeta$ in the (x,x_0) parameter space, as obtained from Eqs. (4.10)–(4.14). The numbers attached to the contours are the values of the derivative. Vertical bars for Li and the pseudometals "Cu," "Ag," and "Au," indicate the ranges of x_0 which can be fitted as described in the text.

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[35] Reference 10, pp. 399 and 488.

[36] See, e.g., Ref. 28, Sec. 1.1.

[37] A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965); see also Ref. 28, Sec. 8.9.

[38] F. Mueller, Phys. Rev. **153**, 659 (1967).

[39] V. Heine, Phys. Rev. **153**, 673 (1967).

TABLE I. Thermopower coefficients for solid monovalent metals in the nearly-free-electron model. Calculated from Eqs. (4.9)–(4.13) for parameters chosen as discussed in Sec. V.

	Li	Na	K	Rb	Cs	"Cu"	"Ag"	"Au"
$(d\ln l/d\ln\epsilon)_\zeta$	−1.09	1.68	1.75	1.77	1.67	−1.67	−0.62	−0.63
ξ	−0.09	2.68	2.75	2.77	2.67	−0.67	0.38	0.37
ξ_{exp}	−6.7[a]	2.7[a]	3.8[a]	2.3[a]	0.2[a]	−1.7[b]	−1.1[b]	−1.5[b]

[a] J. S. Dugdale, Science **134**, 77 (1961).
[b] As quoted in Ref. 12, p. 45.

the Fermi level within a nearly-free-electron picture, and that quantitatively accurate results can be obtained therefrom. Work is presently being done to extend the calculation to Ag and to Au[40]. Consider those two conduction-band states at the point L of the Brillouin zone which border the band gap there just above the Fermi level. The lower of this pair has p-like symmetry (L_2') while the upper is s like (L'). This has long been known for Cu,[41] is now established for Ag,[40,42] and is surely so for Au.[43] This implies that the (111) Fourier coefficient of the effective interaction is positive, and since the deformation potential theorem assures us that the effective electron-ion interaction is negative at $q=0$, it must go through zero. Accordingly, we invent three simple metals whose lattice structures and r_s are those of Cu, Ag, and Au, and fix x_0 for these pseudometals by fitting $V(q)$ to the $V(111)$ extracted by Ziman from de Haas–van Alphen data.[12] We expect in this way to obtain a qualitative indication of the importance of interference effects for the real metals.

The results of all this parameter fitting are displayed, in Fig. 5, in a parameter-space plot of lines of constant $(d\ln l/d\ln\epsilon)_\zeta$ as given by Eqs. (4.10)–(4.14). Lithium and the pseudometal relatives of Cu, Ag, and Au are distinguished qualitatively from other metals in exactly the manner required. A range of parameters obtained from the AHA potentials for the divalent metals is also shown, but only to indicate where polyvalent metals tend to congregate in such a plot; no claim of direct relevance is being made for them. Table I contains the numbers found by fitting for the alkalies to the first zero in the published curves of Animalu and Heine and for the pseudometals as described above. No pretense to quantitative comparison to experiment is to be read into this table, if for no other reason than that the Bragg peak rises in the structure factor have been excised.

The noble metals, of course, present additional complications due to the d bands lying close to and below the Fermi level. The effective interaction of Mueller and of Heine contains, in addition to a weak pseudopotential, terms arising from hybridization and resonancelike interaction with the d bands, and these latter are not properly allowed for in the model $V(q)$ of Eq. (3.1). Since the resonances lie below the Fermi level we may expect them to provide a sizeable *positive* contribution to $(d\ln l/d\ln\epsilon)_\zeta$, and it seems likely that this would be essential to the success of a realistic calculation. Without this effect of the resonances, the Bragg peak rise in the real $S(q)$ would probably lead to negative ξ which were very much too large.

As regards the alkalies, the one puzzling case would seem to be that of Cs, and it should be remarked that for liquid Cs near the melting point $\xi=-1.3$.[22] We emphaize that the discrepancy found here for Cs is *not* due to the use of a Debye structure factor. A detailed calculation has now been made which shows that the thermopowers of all the other alkalies can be understood in terms of simple pseudopotentials with interference effects amplified by realistic structure factors.[44] For example, the reason why Sjundstrom's calculation[25] for liquid Li gave the correct sign is simple: The mean-free-path integral Eq. (4.2) was evaluated numerically and hence the q dependence of $V(q)$ was retained. A possible source of the behavior of Cs appears to be the d bands which in this metal lie close to and *above* the Fermi level.[20] A resonancelike interaction associated with these would give a negative contribution to ξ, and this would moreover be in accord with the effects of pressure on solid Cs.[45,46] Should this prove to be the case, then perhaps Cs should be removed from the list of simple metals.

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[40] R. Jacobs (to be published), cited in Ref. 39 as Ref. 13.

[41] B. Segall, Phys. Rev. **124**, 1797 (1963); G. A. Burdick, *ibid.* **129**, 138 (1963).

[42] B. Segall, Bull. Am. Phys. Soc. **6**, 145 (1961).

[43] F. Mueller (private communication).

[44] J. E. Robinson and J. D. Dow, Bull. Am. Phys. Soc. **12**, 22 (1967); (to be published).

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

[46] M. Tosi and T. Arai, in *Advances in High Pressure Research*, edited by R. S. Bradley (Academic Press Inc., New York, 1966), Vol. I, p. 307.