

eliminates some of the low-frequency phonons which in turn decreases the phonon-enhanced density of states at the lowest temperatures. This would qualitatively account for the decrease of T_c with stress and the decrease in heat capacity. However, it is apparent that much more work will be required before a definitive explanation will be possible.

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Electrical Resistivity of the Simple Metals*

NATHAN WISER†

Department of Physics, University of Illinois, Urbana, Illinois

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A critical discussion is presented of the current status of the calculation of the dc electrical resistivity of simple metals. The general formalism, which has recently been given sound theoretical justification, shows that there are two elements to the calculation: (1) the dynamical structure factor, which describes the deviation of the ionic positions from perfect periodicity, and (2) the matrix elements of the screened electron-phonon interaction. The first element can be obtained directly from experiment. The second element, the crux of the problem, has been calculated by a number of methods, including empirical means and the pseudopotential approach. These methods are shown to be inadequate for resistivity calculations because of the sensitivity of the electrical resistivity to the value of the matrix elements at large momentum transfers. It is demonstrated explicitly that the seemingly small errors present in pseudopotential calculations lead to errors as large as a factor of 2 in the electrical resistivity.

I. INTRODUCTION

THE calculation of the dc electrical resistivity of the simple metals is one of the fundamental problems of solid-state physics. Recent many-body work^{1,2} has shown that for static perturbing fields, the transport coefficients are given correctly by the standard weak-coupling theory³ which has long been used, without any many-body electron-phonon interaction corrections. Therefore, assuming only the validity of the Boltzmann equation,⁴ one can derive an exact expression for the dc electrical resistivity. Baym⁵ gives the following result for a spherical Fermi surface based on the usual³ variational calculation:

$$\rho = \frac{m^2 z}{12\pi^3 n^3 \hbar^3 e^2} \int_0^{2k_F} q^3 dq |v(q)|^2 S(q), \quad (1)$$

where $v(q)$ is the matrix element of the screened elec-

tron-ion interaction and

$$S(q) \equiv \int \frac{d\Omega_{\mathbf{q}}}{4\pi} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{S'(\mathbf{q}, \omega) \beta \omega}{e^{\beta \omega} - 1}. \quad (2)$$

As usual, β is the inverse of kT , z is the number of conduction electrons per ion, n is the density of conduction electrons, k_F is the Fermi momentum, and m is the effective mass without electron-phonon interaction corrections. The quantity $S'(\mathbf{q}, \omega)$ is closely related to $S(\mathbf{q}, \omega)$, the dynamical structure factor of Van Hove⁶ which is defined as the Fourier transform of the time-dependent pair correlation function. The quantity $S'(\mathbf{q}, \omega)$ equals $S(\mathbf{q}, \omega)$ minus the elastic Bragg peaks, which do not scatter electrons and therefore do not contribute to the resistivity. The crux of the problem of calculating ρ lies in the determination of $v(q)$. The quantity $v(q)$ has been determined by a number of methods. We will show that these methods are inadequate for resistivity calculations.

There are two parts to the calculation of the electrical resistivity. First, one must determine $S(q)$, which describes the deviation of the ionic positions from perfect periodicity, and second, one must determine $v(q)$, which describes the scattering of an electron by a single screened ion. We shall consider each of these quantities in turn (Secs. II and III). In Sec. IV, we

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† Present address: IBM Watson Research Center, Yorktown Heights, New York, 10598.

¹ A. B. Migdal, *Zh. Eksperim. i Teor. Fiz.* **34**, 1438 (1958) [English transl.: *Soviet Phys.—JETP* **7**, 996 (1958)].

² R. E. Prange and L. P. Kadanoff, *Phys. Rev.* **134**, A566 (1964).

³ J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1962), Chap. VII and IX.

⁴ W. Kohn and J. M. Luttinger, *Phys. Rev.* **108**, 590 (1957).

⁵ G. Baym, *Phys. Rev.* **135**, A1691 (1964).

⁶ L. Van Hove, *Phys. Rev.* **95**, 249 (1954).

discuss some important features of the integrand of Eq. (1) and demonstrate explicitly that the seemingly small errors present in $v(q)$ lead to substantial errors in ρ . In Sec. V, we give a critique of current resistivity calculations. A summary follows in Sec. VI.

II. DYNAMICAL STRUCTURE FACTOR

It has been shown^{5,6} that $S'(\mathbf{q},\omega)$ can be measured directly by inelastic neutron scattering. At the present time, however, $S'(\mathbf{q},\omega)$ has not been measured in sufficient detail to permit performing the integrations required in Eqs. (1) and (2). Therefore, for the solid phase, we resort to the one-phonon approximation. In this approximation,

$$S'(\mathbf{q},\omega) = \frac{2\pi}{M} \sum_{\lambda} (\mathbf{q} \cdot \hat{e}_{\mathbf{q}\lambda})^2 \delta(\omega^2 - \omega_{\mathbf{q}\lambda}^2) \frac{\omega/\omega_{\mathbf{q}\lambda}}{1 - e^{-\beta\omega}}, \quad (3)$$

where $\hat{e}_{\mathbf{q}\lambda}$ is the polarization vector and $\omega_{\mathbf{q}\lambda}$ is the temperature-independent frequency of the phonon of wave number \mathbf{q} and polarization λ , and M is the ionic mass. We can improve the one-phonon model in two ways. First, we can ascribe a lifetime to the phonons. Numerical evaluation shows that this improvement changes ρ by only a few percent at all temperatures. Second, we can let the phonon frequencies vary with temperature. In the case of Na, the phonon frequencies $\omega_{\mathbf{q}\lambda}$ were measured at 90°K.⁷ Incorporating approximately the temperature variation of the $\omega_{\mathbf{q}\lambda}$ of Na, as estimated by the temperature variation of the elastic constants, changes ρ by about 20% both at high and at low temperatures. Similar results were obtained by Darby and March.⁸ However, the elastic-constant data may lead to an overestimate of the temperature variation of the $\omega_{\mathbf{q}\lambda}$, as has been shown by experiments on Al. The temperature variation of the $\omega_{\mathbf{q}\lambda}$ of Al has been measured by Larsson, Holmryd, and Dahlborg,⁹ who compared their experimental values with the results calculated from the temperature variation of the elastic constants. They found that the calculation overestimates the temperature variation of the $\omega_{\mathbf{q}\lambda}$ of Al by about 50%. If the same holds true for Na, then the maximum error introduced into ρ by assuming that the $\omega_{\mathbf{q}\lambda}$ of Na are temperature-independent is much less than 20%. The two improvements we have discussed take no account of the multiphonon background.

For some metals, ignoring the temperature variation of the $\omega_{\mathbf{q}\lambda}$ gives rise to a larger error in ρ than for Na. In the case of Al, using the $\omega_{\mathbf{q}\lambda}$ measured at an intermediate temperature, say 300°K, as the temperature-independent $\omega_{\mathbf{q}\lambda}$ leads to an error in ρ of about 40% both at

high and at low temperatures. We computed this error from the measured,⁹ not the calculated, temperature variation of the $\omega_{\mathbf{q}\lambda}$ of Al. The values for Na and Al are typical of many metals; the error introduced into ρ by neglecting the temperature variation of the $\omega_{\mathbf{q}\lambda}$ is generally of order 20–40%.

In summary, for some metals, e.g. Na, assuming that the $\omega_{\mathbf{q}\lambda}$ are temperature-independent seems adequate ($\lesssim 20\%$ error in ρ), whereas for other metals, e.g. Al, the temperature variation of the $\omega_{\mathbf{q}\lambda}$ should be taken into account. If this is done, the resulting “improved” one-phonon approximation is adequate to calculate the resistivity at all temperatures except possibly near the melting point where, for certain metals, the multiphonon background may become important. It should be emphasized, however, that one must make no further approximation,¹⁰ such as treating umklapp processes inaccurately, lumping together longitudinal and transverse phonon modes, using an approximate rather than the measured phonon spectrum, etc. Introducing any of these further approximations may easily lead to an error in ρ of a factor of 2 or even more. In particular, the Debye approximation to the phonon spectrum is very poor for calculating ρ .¹⁰

In the liquid phase, we are invariably at high enough temperatures that

$$\beta\omega/(e^{\beta\omega}-1) \approx 1, \quad (4)$$

and therefore, $S(q)$ equals the static atomic structure factor. The validity of Eq. (4) has been verified by Greene and Kohn.¹¹ In the liquid phase, $S(q)$ can be read directly from neutron or x-ray diffraction data.¹² A typical curve of $S(q)$ is shown in Fig. 1. For some metals, x-ray diffraction data are more reliable, whereas for other metals, neutron diffraction data are more reliable. There are recent neutron data¹³ for all the liquid alkalis. However, we should remark on a general difficulty with using the diffraction data to calculate the resistivity. Diffraction data have always been taken in order to obtain the radial distribution function of the liquid. For the monovalent metals, the region $q \lesssim 2k_F$ is rather unimportant in determining the radial distribution function and consequently the experimentalists do not always strive for high accuracy in this region. Therefore, for use in transport theory, the diffraction experiments should be repeated with more emphasis placed on the region $q < 2k_F$. Such experiments are currently being carried out for the alkalis.

Our over-all conclusion is that $S(q)$ poses no problem

⁷ A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. Bowers, *Phys. Rev.* **128**, 1112 (1962).

⁸ J. K. Darby and N. H. March, *Proc. Phys. Soc. (London)* **84**, 591 (1964).

⁹ K.-E. Larsson, S. Holmryd, and U. Dahlborg, in *Inelastic Scattering of Neutrons in Solids and Liquids* (The International Atomic Energy Agency, Vienna, 1961), p. 587.

¹⁰ M. Bailyn, *Phys. Rev.* **120**, 381 (1960).

¹¹ M. P. Greene and W. Kohn, *Phys. Rev.* **137**, A513 (1965).

¹² It should be mentioned that the diffraction data which give $S(q)$ in the liquid phase do not have the Bragg peaks subtracted out. It is assumed that in the liquid phase, except for forward scattering, there is no remanant of the long-range order which gives rise to the Bragg peaks in the solid phase.

¹³ N. S. Gingrich and L. Heaton, *J. Chem. Phys.* **34**, 873 (1961). I wish to thank Dr. Heaton for sending me the numerical data from which their graphs were drawn.

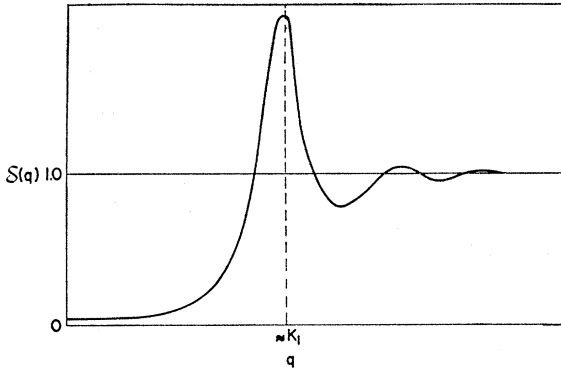


FIG. 1. A typical curve of $S(q)$. The first peak occurs approximately at K_1 , the smallest nonzero reciprocal lattice vector, and $S(0) \approx 0.03$ for the alkalis at the melting temperature.

in calculating the resistivity for either the solid or liquid phase as long as one uses reliable experimental data, rather than resorting to calculations.

III. ELECTRON-ION INTERACTION MATRIX ELEMENTS

For all the simple metals, the curves of the screened electron-ion interaction matrix elements $v(q)$ are qualitative similar; a typical curve is shown in Fig. 2. At $q=0$, $v(q) = -\frac{2}{3}E_F$, and $v(2k_F)$ is near zero. There had been some question about the possibility of large electron-electron interaction corrections to the value of $v(0)$, but it has recently been shown¹⁴ that the only such correction is the insertion of the factor $(m/m^*)_{e1-e1}$, the Landau effective mass which does not include the effects of the electron-phonon interaction. The ratio $(m/m^*)_{e1-e1}$ differs from unity by only about 5% for all metals¹⁵ and even this small correction to $v(0)$ does not appear in the resistivity because all the effective masses cancel in the $q \approx 0$ region of the integral in Eq. (1).

Various methods have been used to determine $v(q)$, including direct calculation,¹⁶ empirical methods,^{11,17} and the pseudopotential formalism. The pseudopotential formalism describes the scattering of electrons in terms of pseudo-wave functions and the pseudopotential rather than in terms of the true wave functions and the true electron-ion potential. This transformation has been clearly described by Austin, Heine, and Sham¹⁸ and we quote their Eq. (42) for the scattering amplitude $W(\mathbf{k}, \mathbf{k}+\mathbf{q})$, which is equivalent to the matrix element

$v(q)$ in the case of a spherical Fermi surface,

$$W(\mathbf{k}, \mathbf{k}+\mathbf{q}) = (\phi_{\mathbf{k}} | V_p | \phi_{\mathbf{k}+\mathbf{q}}) - \sum_c (\phi_{\mathbf{k}} | \psi_c) (\psi_c | V_p | \phi_{\mathbf{k}+\mathbf{q}}), \quad (5)$$

where V_p is the screened pseudopotential, $\phi_{\mathbf{k}}$ is the properly normalized pseudo-wave function, $|\mathbf{k}| = |\mathbf{k}+\mathbf{q}| = k_F$, and the sum is taken over all the core states ψ_c . Austin, Heine, and Sham point out that in practice the second term may be neglected because V_p is nearly zero in the core region where ψ_c is nonzero. Furthermore, the pseudo-wave function is well represented by a single plane wave in the liquid phase. Even in the plane-wave approximation, the calculation of the matrix elements is not trivial because V_p is a nonlinear operator, rather than a simple potential. Harrison¹⁹ has recently calculated matrix elements of V_p between plane-wave states, both lying on the Fermi surface; this is exactly what is needed to calculate ρ . The normalization of Harrison's plane waves differs from the normalization required of the pseudo-wave functions in Eq. (5), but this difference can be ignored because it leads to an error in $v(q)$ of only about 10%, which is smaller than other errors in this calculation.

IV. CALCULATION OF THE RESISTIVITY

We now turn to the actual calculation of ρ . Ziman¹⁷ has pointed out a distinction between the monovalent and the polyvalent metals which stems from the form of the $S(q)$ curve. As shown in Fig. 1, the first peak of $S(q)$ occurs at approximately K_1 , the smallest, nonzero reciprocal lattice vector, whose magnitude does not depend on valence, but the integration over q in Eq. (1) is carried out to $2k_F$, which does depend on valence. For the monovalent metals, $2k_F < K_1$ and only the shoulder of the first peak of $S(q)$ is included in the integration and, therefore, $S(q)$ rises sharply near $2k_F$. The q^3 factor also weights the integrand strongly toward $2k_F$. Although $|v(q)|^2$ decreases as q increases and, in fact, passes through zero near $2k_F$, the net effect of all three factors is to make the high- q region dominate the integral. It is also true for the polyvalent metals that the high- q region makes the largest contribution to the q integration, even though the first peak of $S(q)$ occurs at a smaller value of q/k_F .

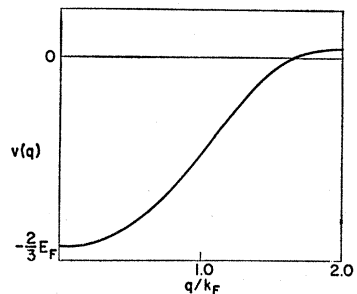


FIG. 2. A typical curve of $v(q)$ for a simple metal.

¹⁴ V. Heine (unpublished). For an explicit derivation, based on the Landau theory of Fermi liquids, see D. Pines and P. Nozieres, *Theory of Quantum Liquids* (W. A. Benjamin, Inc., New York, 1966), Part I.

¹⁵ T. M. Rice, *Ann. Phys. (N. Y.)* **31**, 100 (1965).

¹⁶ J. Bardeen, *Phys. Rev.* **52**, 688 (1937).

¹⁷ J. M. Ziman, *Phil. Mag.* **6**, 1013 (1961); *Advan. Phys.* **13**, 89 (1964), Sec. 7.

¹⁸ B. J. Austin, V. Heine, and L. J. Sham, *Phys. Rev.* **127**, 276 (1962).

¹⁹ W. A. Harrison, *Phys. Rev.* **131**, 2433 (1963).

In view of the foregoing discussion, we wish to emphasize the following point. In the dominant high- q region, $v(q)$ is fairly small, and therefore small absolute errors, of order 0.01–0.02 Ry, constitute large *percentage* errors in $v(q)$ and will lead to a substantial error in ρ .

To illustrate this point, we have taken Harrison's^{19,20} pseudopotential matrix elements for $v(q)$ and calculated ρ for several liquid metals. The main advantage of performing the calculation for the liquid phase is that, to an excellent approximation, the Fermi surfaces of liquid metals are spherical and therefore we may use Eq. (1), which has been specialized to the case of a spherical Fermi surface. In the case of a nonspherical Fermi surface, the pseudo-wave functions are not plane waves, and therefore, the expression for ρ contains an additional summation and more complicated angular integrations. Harrison estimates that the error in his $v(q)$ curves is about 0.01–0.02 Ry. We shall see explicitly what the effect is on ρ of an error in $v(q)$ of 0.015 Ry.

There are five metals for which both Harrison's pseudopotential matrix elements²¹ and also neutron or x-ray diffraction data for the liquid²² are available. These metals are: Li, Na, K, Zn, and Al. The results of the calculation of the resistivity using these data are shown in Table I, together with the experimental values.²³ Note that the over-all agreement between theory and experiment is not particularly good, but this is not the point here. We are interested in the sensitivity of ρ to errors in $v(q)$. We have estimated this sensitivity by varying $v(q)$ by ± 0.015 Ry in the important region $k_F < q < 2k_F$ and repeating the calculation of ρ . The results are shown in Table I in the columns labeled ρ_+ and ρ_- . Since Harrison's $v(q)$ are accurate to about 0.015 Ry, either of the ratios $|\rho_{\pm} - \rho_{\text{calc}}|/\rho_{\text{calc}}$ gives an estimate of the percentage error of ρ_{calc} . We see that the error is large, particularly

²⁰ In a subsequent paper [Phys. Rev. 136, A1107 (1964)], Harrison recalculated the pseudopotential matrix elements for Na, Al, and Mg by electronic computer, using a somewhat modified pseudopotential. The results were similar to his earlier hand calculation (Ref. 19). Since the difference between the numbers which result from these two calculations is within the error of each and the later calculations do not cover all the metals we wish to treat, we shall use the results of the earlier calculation exclusively.

²¹ The pseudopotential matrix elements given in Harrison's Table I (Ref. 19) were calculated at the electron density appropriate to $T=0^\circ\text{K}$. We adjusted them to the electron density appropriate to the temperature at which the diffraction data were taken by means of a modification of the method described by Harrison in Sec. IV of his paper. We used Harrison's Eq. (4) and assumed that β is independent of density, but we did not assume that β is independent of q .

²² The neutron data for Li, Na, and K are from Ref. 13. The x-ray data for Al and Zn are from C. Gamertsfelder, J. Chem. Phys. 9, 450 (1941). Note that the x-ray data are 25 years old.

²³ The experimental values for Zn and Al were taken from A. Roll and H. Motz, Z. Metallk. 48, 272 (1957) and the experimental values for the alkalis were taken from S. M. Kapelner and W. D. Bratton, Pratt and Whitney Technical Report No. PWAC-376 (Middletown, Connecticut, 1962). The latter document can be purchased for 75¢ from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

TABLE I. Experimental and calculated values of the electrical resistivity of liquid metals. The units for ρ are $\mu\Omega\text{ cm}$.

Metal	Temp. (°C)	ρ_{expt}	ρ_{calc}	ρ_+ ^a	ρ_- ^a	Error of ρ_{calc} ^b (%)	ρ (Sundström) ^c
Li	180	25	22	31	24	40	17
Na	100	9.7	22	13	43	100	9.4
K	65	14	123	49	237	90	32
Zn	460	37	36	38	37	6	44
Al	700	25	40	50	35	25	25.

^a ρ_{\pm} is the resistivity calculated with $v(q) \rightarrow v(q) \pm 0.015$ Ry in the region $k_F < q < 2k_F$.

^b By "error of ρ_{calc} " we mean the larger of the two ratios $|\rho_+ - \rho_{\text{calc}}|/\rho_{\text{calc}}$.

^c The calculated values of Sundström are taken from Table 3 of Ref. 28.

for the monovalent metals. By changing the matrix element from $v(q) - 0.015$ Ry to $v(q) + 0.015$ Ry, we change ρ by more than a factor of 3 for Na and by almost a factor of 5 for K. Energy changes of order 0.015 Ry are fairly small on the traditional energy scale of metals (only 2–10% of E_F), but nevertheless, the effect on ρ of such an error is quite substantial. It is clear that pseudopotential matrix elements are not yet accurate enough for electrical resistivity calculations.

We wish to emphasize that we are *not* implying that Harrison's pseudopotential matrix elements are too inaccurate for any purpose. In fact, Harrison has made detailed calculations²⁴ of a number of electronic properties of several metals and found generally good agreement between theory and experiment. However, the electrical resistivity is particularly sensitive to $v(q)$ and the presently available pseudopotential matrix elements are inadequate for determining the resistivity, even though they may lead to good results elsewhere.

V. DISCUSSION OF PREVIOUS WORK

We wish to discuss three recent papers which report calculations of the electrical resistivity. The general formalism and point of view of all three papers is the same; they differ in their manner of determining $v(q)$. We begin with the work of Ziman,¹⁷ who was the first to derive the high-temperature limit of Eq. (1) and applied it to a qualitative discussion of liquid monovalent metals. In the absence of detailed knowledge of $v(q)$, Ziman suggested the following empirical approach. He separated $v(q)$ into v_I and v_{II} , where v_I (called the plasma term) arises primarily from the screening of the long-range Coulomb potential by the conduction electrons, and v_{II} (called the structure term) arises from the detailed structure of the ionic core. He equated v_I to $-\frac{2}{3}E_F f(q)$, where $f(q)$ is some function which equals unity at $q=0$ and approaches zero as $q \rightarrow 2k_F$, and he approximated v_{II} in the region of q near $2k_F$ by the constant $v(K_1) = \frac{1}{2}E_{\text{gap}}$, where K_1 is the smallest non-zero reciprocal lattice vector and E_{gap} is the band gap

²⁴ W. A. Harrison, Phys. Rev. 129, 2512 (1963); 136, A1107 (1964).

at the nearest zone face. For small q , $v_{II} \approx 0$ because of screening. Ziman stressed that the separation of $v(q)$ into v_I and v_{II} is arbitrary but has the useful property that for small q (plasma region), $v_{II} \approx 0$, whereas for q near $2k_F$ (structure region), $v_I \approx 0$. Moreover, in the plasma region, $S(q) \approx S(0) \propto kT$, whereas in the structure region $S(q)$ rises sharply.²⁵ Therefore, he split ρ into ρ_I and ρ_{II} , the two parts coming from the plasma region and structure region of the q integration in Eq. (1), respectively. He showed that $\rho_I \propto kT$ and $\rho_{II} \propto \langle S \rangle_{av} (E_{gap})^2$. Ziman then stated that for Na the band gaps are so small that one may disregard ρ_{II} entirely: $\rho(\text{Na}) \approx \rho_I(\text{Na})$. On this basis he developed a qualitative theory of the electrical resistivity of liquid Na, discussing the temperature dependence of ρ , the change of resistivity on melting, and other properties, finally extending the work to the other alkalis as well. However, inserting numbers into Eq. (1) shows that for any reasonable $v(q)$, $\rho_{II}(\text{Na}) > \rho_I(\text{Na})$ ²⁶ even though Na has a negligibly small band gap. Thus, the Ziman analysis of Na has turned out to include only the smaller term. Moreover, the variation of $v(q)$ near $2k_F$ is very important and the approximation $v(q) \approx v(K_1)$ is inadequate. In fact, no calculation of ρ can succeed unless $v(q)$ is determined accurately in the critical region near $2k_F$.

This brings us to the second paper we wish to discuss, that of Greene and Kohn¹¹ (G-K). They calculated ρ for Na at all temperatures in both the liquid and solid phases. G-K determined $S(q)$ from experiment, using the one-phonon approximation in the solid, and expressed $v(q)$ in terms of phase shifts η_l , two of which they tried to determine empirically. With slight modifications,²⁷ their Eq. (5.2) is

$$v(q) = -(4E_F/3\pi) \sum_l \bar{\eta}_l P_l(1 - q^2/2k_F^2), \quad (6)$$

where $P_l(x)$ is the Legendre polynomial of order l and $\bar{\eta}_l \equiv (2l+1)\eta_l$. G-K made preliminary calculations which show that the magnitude of the phase shifts decreases rapidly with increasing l and, in fact, $\bar{\eta}_3$ is already fairly small. Therefore, G-K truncated the sum at $l=3$ and used their calculated value for $\bar{\eta}_3$. Of the remaining parameters ($\bar{\eta}_0$, $\bar{\eta}_1$, and $\bar{\eta}_2$), one is fixed by the Friedel sum rule,

$$\sum_l \bar{\eta}_l = \frac{1}{2}\pi, \quad (7)$$

²⁵ As Ziman explained, this statement limits the discussion to the monovalent liquid metals.

²⁶ We took $q = 1.3k_F$ as a reasonable point at which to split the q integration into the plasma resistance region and the structure resistance region. If we had chosen a value of q larger than $1.3k_F$, then in the plasma region the approximation $S(q) \approx S(0)$, which is crucial to the Ziman analysis, would no longer be valid. Using the neutron diffraction data at 100°C, the ratio $\rho_{II}(\text{Na})/\rho_I(\text{Na})$ equals 1.7, 1.2, and 2.8, using Harrison's pseudopotential (Ref. 19), Sundström's calculation (Ref. 28), and the G-K phase-shift analysis (Ref. 11), respectively.

²⁷ We have divided the G-K equation for $v(q)$ by the atomic volume to conform to our $v(q)$ and we have neglected the effective-mass correction because all the masses cancel in the phase-shift expression for ρ . Also, we have introduced the notation $\bar{\eta}_l$ to simplify the later discussion.

which is equivalent to the statement $v(0) = -\frac{2}{3}E_F$. Thus, G-K reduced the problem of finding $v(q)$ for all q to the problem of finding two q -independent parameters, say $\bar{\eta}_0$ and $\bar{\eta}_1$; these were to be determined empirically. Substituting Eq. (6) into Eq. (1) and performing the q integration yields an expression of the form

$$\rho = \sum_{i,l} A_{il}(T) \bar{\eta}_i \bar{\eta}_l, \quad (8)$$

where $A_{il}(T)$ contains the temperature dependence of ρ . The plan of G-K was the following. For any given temperature, Eq. (8) represents an ellipse in $\bar{\eta}_0, \bar{\eta}_1$ space. Therefore, one chooses several different temperatures, plots the corresponding ellipses, and their common point of intersection fixes $\bar{\eta}_0$ and $\bar{\eta}_1$. However, G-K found that there was no common point of intersection. Therefore, they resorted to their calculated values of $\bar{\eta}_0$ and $\bar{\eta}_1$ (which did correspond to a point on one of the ellipses) and proceeded to calculate ρ at various temperatures. The discrepancy between theory and experiment was worst at low temperatures where it exceeded a factor of 2.

In a note added in proof, G-K report that they improved the one-phonon approximation by letting the phonon frequencies vary with temperature, as estimated by the temperature variation of the elastic constants. This alters $A_{il}(T)$, which in turn alters the ellipses, and their method now does lead to values for $\bar{\eta}_0$ and $\bar{\eta}_1$. Using the values of $\bar{\eta}_0$ and $\bar{\eta}_1$ so determined and the improved $A_{il}(T)$, G-K obtain agreement between theory and experiment to within 20% over the entire temperature range in the solid phase. From this result, they conclude that the one-phonon approximation is inadequate for Na. This interpretation should be clarified. The change in ρ of a factor of 2 which G-K found at low temperatures when they included the temperature variation of the phonon frequencies stemmed primarily from the modified values of $\bar{\eta}_0$ and $\bar{\eta}_1$, rather than from the modified values of $A_{il}(T)$. In fact, using G-K's modified phase shifts ($\bar{\eta}_0 = 0.524$, $\bar{\eta}_1 = 0.774$, $\bar{\eta}_2 = 0.168$, $\bar{\eta}_3 = 0.105$) and the *unmodified* values of $A_{il}(T)$, i.e., assuming temperature-independent phonon frequencies, also results in 20% agreement between theory and experiment for ρ both at high temperatures (273°K) and at low temperatures (40°K). Of course, if one wishes to calculate ρ to better than 20% accuracy [or the ratio $\rho(T \approx T_m)/\rho(T \approx 0^\circ\text{K})$ to better than 40% accuracy], then even for Na the one-phonon approximation must be improved, as G-K have pointed out.

We can uncover a difficulty with the application of the G-K method by studying Eq. (6). At $q = 2k_F$, the argument of the Legendre polynomials is -1 . Using the fact that $P_l(-1) = (-1)^l$, we have

$$v(2k_F) = -(4E_F/3\pi) \sum_l (-1)^l \bar{\eta}_l. \quad (9)$$

We combine Eqs. (7) and (9) and for $\bar{\eta}_3$ we insert its

calculated value, $\bar{\eta}_3=0.105$, to obtain

$$v(2k_F) = -(8E_F/3\pi)(0.68 - \bar{\eta}_1). \quad (10)$$

The value of $\bar{\eta}_1$ which G-K used in their original calculation was $\bar{\eta}_1=0.62$. From Eq. (10), the percentage error in $v(2k_F)$ is seen to be ten times as large as the percentage error in $\bar{\eta}_1$. We feel that because of this magnification of errors in the important region of q , the G-K method is not practical for calculating ρ . However, perhaps the method could be successfully modified to avoid the unfortunate cancellation which appears in Eq. (10).

Finally, we turn to the work of Sundström.²⁸ She used the model pseudopotential of Heine and Abarenkov,²⁹ who determined the unscreened pseudopotential from spectroscopic data of the free ions, rather than by direct calculation. For those five metals for which our work overlaps, we give her results in the last column of Table I. The error in the Heine-Abarenkov pseudopotential³⁰ is comparable to the error in Harrison's pseudopotential. Correspondingly, Sundström's calculated values for ρ are comparable to, although somewhat better than, those obtained using Harrison's pseudopotential. For illustrative purposes, we plot in Fig. 3 the pseudopotentials of Heine-Abarenkov and of Harrison for Na, together with the $v(q)$ which results from the G-K phase-shift analysis. We see that the three curves are

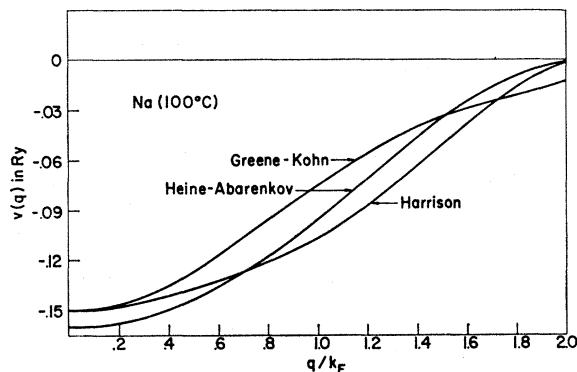


FIG. 3. The screened, electron-ion interaction matrix elements of Greene-Kohn, Heine-Abarenkov, and Harrison for Na at the density appropriate to 100°C. At this density, $-\frac{2}{3}E_F = -0.150$ Ry. For the Heine-Abarenkov curve, $v(0)$ is slightly less than this value because of the inclusion of effective-mass and orthogonality corrections.

²⁸ L. J. Sundström, *Phil. Mag.* **11**, 657 (1965). I wish to thank Dr. Neil Ashcroft for sending me the numerical data which Dr. Sundström used in her calculations.

²⁹ V. Heine and I. Abarenkov, *Phil. Mag.* **9**, 451 (1964).

³⁰ N. W. Ashcroft and L. J. Guild, *Phys. Letters* **14**, 23 (1965).

similar; they never differ by more than 0.03 Ry and usually by much less. Yet, the resistivities calculated from the three curves differ by more than a factor of 2.

We mention in passing the recent work of Darby and March.⁸ They calculated the resistivity of solid Na as a function of temperature and report excellent agreement with experiment. However, Darby and March have reserved the description of their calculation of the electron-ion interaction matrix elements for a later publication.

VI. SUMMARY

From a qualitative point of view, the calculation of the electrical resistivity is well in hand. The general theory has now been put on firm basis. We see that there are two ingredients to the calculation, viz., the matrix elements of the screened electron-ion interaction and the dynamics of the ions, and each of these is well understood, at least in principle. However, from a quantitative point of view, the present status of resistivity calculations is less encouraging. To obtain the structure factor $S(q)$, one must turn to experiment. The one-phonon approximation, improved for some metals by including the temperature variation of the phonon frequencies, seems adequate in the solid at temperatures not too near the melting temperature, with the provisos that one make no further approximation and that one use the experimentally determined phonon spectrum. In the liquid, one may use the x-ray or neutron diffraction data. However, these experiments should be repeated with an eye to increased accuracy in the region $q < 2k_F$. The main problem lies in the determination of the matrix elements $v(q)$. The calculation of ρ is very sensitive to $v(q)$ in the region of q near $2k_F$. This sensitivity demands that one exercise great care in employing empirical methods to determine $v(q)$. The pseudopotentials currently available contain errors large enough to lead to a 40–100% error in ρ for the alkalis. We are forced to conclude that in general quantitative agreement between theory and experiment has not yet been achieved in electrical-resistivity calculations.

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