Table VIII gives the measured values for the compounds studied. The last column is defined by the equation $Q=M_q/\sqrt{3}\epsilon$, where ϵ is the electronic charge. Thus Q represents the effective charge in electrons equivalent to the measured intensities. (Since the vibrations are triply degenerate, M_q represents the vector sum of the transition moments for the individual components and the factor $1/\sqrt{3}$ must be incorporated to yield the correct value for a single axis. The effect of refractive index was neglected.)

It may be shown by a semiclassical calculation that the polarization per unit volume and hence the intensities of a set of weakly coupled harmonic oscillators are equal to those of an isolated, uncoupled set of equal density. The computed values are in the range of 2ϵ as expected for oxide ion vibrations.

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Influence of Exchange and Correlation on Electron Transport in Metals*

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A result of the collective treatment of Bohm and Pines is that the dependence of electron energy ϵ on the wave vector k differs from that for noninteracting free electrons. It follows that the expressions for those properties, such as conductivity and thermoelectric power, which depend on the relationship between ϵ and k must be suitably modified. Electrical and thermal conductivity are altered in the same manner, suffering slight changes because of changes of the density of states at the Fermi energy and of the relaxation time. The Wiedemann-Franz ratio remains unaltered. For the alkali metals the calculated thermoelectric power is reduced slightly below the free-electron value. The changes in both conductivity and thermoelectricity are too small to permit quantitative comparison with experiment.

I. INTRODUCTION

In a series of papers[1] Bohm and Pines have developed a new method for treating exchange and correlation effects in an electron gas. It was found that the influence of exchange and long-range correlation on the one-electron energies results in an energy *versus* wave vector relationship which is somewhat different from that given by the Hartree approximation. The collective description of electron interaction appears to be much superior to the Hartree-Fock approximation which neglects correlation of electrons with antiparallel spins and leads to incorrect results. In particular, near the Fermi energy the following relation holds[2]

$$\epsilon(k)=\frac{3.68k^2}{r_s^2}(m/m^*)-\frac{0.611}{r_s}\times\left[1-2\beta+\frac{\beta^2+3k^2-1}{2k}+\frac{1-k^2}{k}\ln\left(\frac{1+k}{\beta}\right)\right],\tag{1}$$

where ϵ is in rydbergs, r_s is the average interelectronic distance in units of the Bohr radius, and k is the wave vector in units of k_F, k_F being the wave vector at the Fermi energy. β is a parameter in the theory of Bohm and Pines which is a measure of the screening of the Coulomb interaction. Its value is given by $\beta=0.353\sqrt{r_s}$.[3] Equation (1) is to be compared with the free-electron expression

$$\epsilon_0(k)=\frac{3.68k^2}{r_s^2}\left(\frac{m}{m^*}\right).\tag{2}$$

The purpose of this note is to consider what changes appear in the expressions for the transport properties of an electron gas when Eq. (1) is used in place of the more common Eq. (2).

II. CONDUCTIVITY

The electrical and thermal conductivities of a metal are proportional to the density of states at the Fermi energy, $N(\epsilon_F)$, and to the relaxation time, τ.

The dependence of the relaxation time on the relationship between ϵ and k is a function of the type of scattering (lattice or impurity) and of the temperature. For lattice scattering in the high-temperature limit, an examination of the standard calculation of relaxation time[4] shows that

$$\tau=Dk\left(\frac{d\epsilon}{dk}\right)^2\Big/\frac{d^2\epsilon}{dk^2},\tag{3}$$

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[1] D. Bohm and D. Pines, Phys. Rev. **82**, 625 (1951); **85**, 836 (1952); **92**, 609 (1953); D. Pines, Phys. Rev. **92**, 626 (1953).

[2] The term involving $\beta^3/6$ which appears in D. Pines, Report to the Solvay Congress, Eq. (28), has been omitted in Eq. (1) because it is a higher-order term which is canceled by other higher-order corrections. The author would like to thank Dr. Pines for informing him of this result before publication.

[3] D. Pines, private communication.

[4] A. H. Wilson, *Theory of Metals* (Cambridge University Press, London, 1953), second edition, p. 263.

TABLE I. Conductivity and thermoelectric power of the alkali metals.

	Li	Na	K	Rb	Cs
r_s	3.22	3.96	4.87	5.18	5.57
(m^*/m)[a]	1.45	0.98	0.93	0.89	0.83
β	0.634	0.703	0.78	0.80	0.834
$N(\epsilon_F)/N_0(\epsilon_F)$	0.837	0.90	0.935	0.945	0.965
τ/τ_0	1.28	1.08	0.96	0.93	0.89
σ/σ_0	1.07	0.97	0.90	0.88	0.86
S/S_0	0.83	0.90	0.93	0.94	0.95

[a] Calculated by H. Brooks, quoted by D. Pines, Phys. Rev. **95**, 1090 (1954).

where D is a constant which depends on the atomic mass of the metal, the Debye temperature, the lattice parameter, and the strength of the electron-lattice interaction. Bardeen and Pines[5] have investigated the electron-lattice interaction in the Bohm-Pines collective description and have found that the effective matrix element for the electron-phonon interaction is identical, for wavelength of interest in conduction phenomena, with that found previously by Bardeen[6] using a self-consistent field method which neglects exchange and correlation effects. The constant D in Eq. (3) is, therefore, not altered when exchange and correlation are included.

Substitution of Eq. (2) into Eq. (3) leads to the well-known dependence of the relaxation time on $\epsilon^{\frac{3}{2}}$. From Eq. (1), one finds

$$(d\epsilon/dk)_{\epsilon_F}\equiv X_1=2A+B[\tfrac{1}{2}\beta^2-2+2\ln(2/\beta)] \qquad (4)$$

and

$$(d^2\epsilon/dk^2)_{\epsilon_F}\equiv X_2=2A+B[3-\beta^2-2\ln(2/\beta)], \qquad (5)$$

where $A=(3.68/r_s^2)(m/m^*)$ and $B=0.611/r_s$.

The fractional change in the density of states at the Fermi energy, $N(\epsilon_F)/N_0(\epsilon_F)$, is given by

$$N(\epsilon_F)/N_0(\epsilon_F)=2A/X_1. \qquad (6)$$

This ratio also gives the relative change in the electronic specific heat, C/C_0, and its values for the alkali metals are listed in the fourth row of Table I.

The ratio of the calculated relaxation time to the free-electron value, τ/τ_0, was obtained for each alkali metal by substitution of the parameters in the first three rows of Table I into Eqs. (4), (5), and (3). These ratios are listed in the fifth row of Table I, and in the sixth appear σ/σ_0, the ratios of the calculated electrical conductivities to the free-electron conductivities in the high-temperature limit. Although the changes are significant, in the sense that they could easily be detected, there are, unfortunately, other uncertainties in the theory of electronic conduction in metals which prevent quantitative comparison with experiment.

The fractional change of the thermal conductivity due to exchange and correlation is identical to that of the electrical conductivity, since again only the change due to the relaxation time and the density of states is involved. It follows, therefore, that the Wiedemann-Franz ratio is not affected by these considerations. (A statement to the contrary by Kohler[7] is in error.)

III. THERMOELECTRIC POWER

The absolute thermoelectric power of a metal is given by[8]

$$S=\frac{\pi^2k_0^2T}{3e}\left(\frac{d(\ln N\tau k^2)}{d\epsilon}\right)_{\epsilon_F}, \qquad (7)$$

where e is the charge of the electron and k_0 is Boltzmann's constant. From Eqs. (2), (3), and (7) one readily obtains the well-known result

$$S_0=\pi^2k_0^2T/e\epsilon_F, \qquad (8)$$

since in the free-electron approximation the logarithmic derivative is just $3/\epsilon_F$.

It can be shown by a bit of manipulation that when Eq. (1) is used

$$\left(\frac{d(\ln N\tau k^2)}{d\epsilon}\right)_{\epsilon_F}=(5/X_1)+(X_2/X_1^2)+Bf(\beta)/X_1X_2, \qquad (9)$$

where $f(\beta)=3\beta^2-8+6\ln(2/\beta)$.

The last row of Table I lists S/S_0 for the alkali metals. The ratio S/S_0 is of the same order of magnitude as σ/σ_0, and the comment regarding quantitative comparison with experiment applies here all the more. The present theory of the thermoelectric effects in metals is unable to account for many of the phenomena even qualitatively. Thus, for example, the absolute thermoelectric power of Li and Cu are positive although the free-electron model predicts the opposite sign. From the rather small influence of exchange and correlation on thermoelectricity it follows that this refinement in the theory does not provide a mechanism for explaining these anomalies.

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[5] J. Bardeen and D. Pines (to be published).

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

[7] M. Kohler, Abhandl. braunschweig. wiss. Ges. **5**, 48 (1953).

[8] See reference 4, p. 204.