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IDEAL ELECTRICAL RESISTIVITY OF ALKALI METALS

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The temperature dependence of the ideal electrical resistivity of alkali metals is theoretically investigated using various screened pseudopotential approximations for electron-ion scattering. The structure factor of the ion system is obtained in the one-phonon approximation from the phonon dispersion relations deduced on Sharma and Joshi's model modified by incorporating angular ion-ion interactions of type proposed by de Launay and Clark et al. The calculated resistivities show reasonably good agreement with experiments, except for lithium at very low temperatures.

1. *Introduction*

It is an interesting problem in solid state physics to calculate accurately the electrical resistivity of simple metals. The problem is by no means straightforward, and has been the subject of investigation by many workers since 1928, when Bloch [1] first accounted for the qualitative features of the electrical resistance of metals. The first satisfactory approach to the problem was given by Bardeen [2] who calculated the electrical resistivity of monovalent metals from first principles. Bardeen made use of a simple Debye model for the phonon spectrum and assumed the electronic behaviour to be free electron like because of inadequate knowledge of these quantities in those days.

Considerable effort has been devoted in recent years to improve upon these approximations in the calculation of electronic transport properties of metals. Many workers, notably Ziman [3], Bailyn [4], Bross and Holz [5], and Hasegawa [6] have developed variational approach in studying the transport coefficients of alkali metals by taking into account detailed phonon spectrum and simplified models for electronic band structure. Greene and Kohn [7] have used a phase shift analysis for differential scattering cross section for electron-ion scattering to carry out detailed calculations of the temperature dependence of electrical resistivity of sodium. In spite of several sophistications (e.g., Umklapp processes,

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many-body effects, time-dependent effects, and dynamics of ions from neutron data), the agreement of the theory and experiments is not encouraging. In the recent years, the method of pseudopotentials [8] has proved to be an elegant theoretical framework for the calculation of various properties of simple metals. With the advent of reasonable pseudopotentials and the structure factors, there has been increasing interest in the pseudopotential study of the transport properties of metals at various levels of consistency and sophistication [9–14]. The advantage of the pseudopotential approach lies in the fact that it permits one to take into account the Umklapp processes and coupling to transverse phonons without considering intermediate description of lattice vibrations in terms of phonons.

Resistance to the transport of electricity and heat in pure metals is mainly caused by the scattering of conduction electrons by the thermal motions of the ionic lattice. The theory of the ideal (intrinsic) electrical resistivity, a characteristic property of metals, has been given by many authors, in details, by Ziman [15] and Baym [16]. In Ziman–Baym theory, these transport coefficients depend on two main elements, namely, the electron-ion pseudopotential matrix element $V(\mathbf{q})$ describing electron-ion core scattering and the dynamical structure factor $S(\mathbf{q}, \omega)$ of the ion system. The theoretical study of the transport properties hinges on the evaluation of these two quantities on suitable models. In the one-phonon approximation, the dynamical structure factor is directly related to the phonon spectrum and can be determined from various models for the lattice dynamics of metals.

In the present paper, we report a calculation of the ideal electrical resistivity of alkali metals as a function of temperature using various screened pseudopotential approximations for electron-ion scattering and modified form of Sharma and Joshi's model [17], which includes angular forces [18, 19] between ions, for the phonon dispersion relations. The form factors of the electron-ion pseudopotential are obtained from the Heine and Abarenkov [20] model, Shaw [21] model and its modification by Shyu et al. [22], Bortolani and Calandra [23] model, Giuliano and Ruggeri [24] model, Lee and Heine [25] model, Schneider and Stoll [26] model, Ashcroft [27] model, Sharma and Srivastava [28] model, and Bardeen [2] model. The Giuliano and Ruggeri atomic form factors are taken from the tabulation of Cubiotti et al. [29]. The dynamical structure factors of the ion system are determined in the one-phonon approximation from the phonon spectrum derived by modified Sharma and Joshi's model including angular forces. The choice of alkali metals for this study is motivated by the fact that they are the simplest of bcc metals and appear to approximate well to the free electron model of a metal. By contrast with other metals, they have been studied by many theoretical workers, particularly in regard to several properties. Further, the electrical resistivity and elastic constants of these metals have been the subject of extensive experimental investigations by many workers.

2. *Theory*

Ziman [15], Baym [16], and Greene and Kohn [7] have given general derivation of the ideal electrical resistivity of simple metals caused by scattering of conduction electrons by lattice vibrations from a variational solution of the Boltzmann equation. In the relaxation time approximation, the ideal electrical resistivity ϱ_i can be written as [15]

$$\varrho_i = \frac{m}{nZe^2}\tau_e^{-1}, \tag{1}$$

where m is the bare electron mass, e — the electronic charge, n — the number of ions per unit volume, and Z — the valence of the metal. In the pseudopotential approximation and using the simplest trial function, for lattices with cubic symmetry, the relaxation time τ_e for electron scattering by lattice oscillations is given by [16]

$$\tau_e^{-1} = \frac{3\pi}{2\hbar m k_F^2 S_F^2}\iint \frac{dS_k}{v_k}\frac{dS_{k'}}{v_{k'}}\, q^2 |\langle \boldsymbol{k}'|V|\boldsymbol{k}\rangle|^2 \int\limits_{-\infty}^{\infty} \frac{\beta\omega}{1-e^{-\beta\omega}} S(\boldsymbol{q}, \omega)d\omega, \tag{2}$$

where $\beta = \hbar/k_B T$ and $\boldsymbol{q} = \boldsymbol{k}'-\boldsymbol{k}$ is the scattering vector. Here $\boldsymbol{k}$ and $\boldsymbol{k}'$ are the electron wave vectors defining the one-particle initial and final states, v_k — the electron velocity in the state $\boldsymbol{k}$, k_F — the Fermi wave vector, and S_F — the area of the Fermi surface. $\langle \boldsymbol{k}'|V|\boldsymbol{k}\rangle$ is the pseudopotential matrix element describing the scattering of electron from state $\boldsymbol{k}$ to state $\boldsymbol{k}'$ both on the Fermi surface with the absorption of a phonon of energy $\hbar\omega$ and momentum $\hbar\boldsymbol{q}$. The two surface integrals extend over the Fermi surface. $S(\boldsymbol{q}, \omega)$ is the dynamical structure factor introduced by van Hove [30] and is the Fourier transform of the time-dependent pair correlation function, viz.,

$$S(\boldsymbol{q}, \omega) = \frac{1}{2\pi N}\int\limits_{-\infty}^{\infty} e^{i\omega t}\left\langle \sum_{i,j=1}^{N} e^{-i\boldsymbol{q}\cdot \boldsymbol{r}_i(t)} e^{i\boldsymbol{q}\cdot \boldsymbol{r}_j(0)} \right\rangle_T \tag{3}$$

where $\langle \ldots \rangle_T$ represents a thermal average at temperature T, $\boldsymbol{r}_i(t)$ is the position vector of the i-th ion at time t, N is the total number of ions and the summation is over all the ions in the lattice. The spectral function $S(\boldsymbol{q}, \omega)$ contains necessary information about the dynamics of ions and provides a measure of the density fluctuations in the lattice. For a spherical geometry of the Fermi surface and assuming that the matrix element $\langle \boldsymbol{k}'|V|\boldsymbol{k}\rangle$ is a function of q alone, the two surface integrals can be changed into a three-dimensional integral over $\boldsymbol{q}$ by using the result

$$\iint\limits_{\text{F.S.}} dS_k dS_{k'} \to 2\pi k_F^2 \int \frac{d^3k}{q}. \tag{4}$$

This gives

$$\tau_e^{-1} = \frac{3}{16\hbar m v_F^2 k_F^4}\int\limits_0^{2k_F} S(\boldsymbol{q})\,|V(q)|^2 q^3 dq d\Omega, \tag{5}$$

with

$$S(\boldsymbol{q}) = \int\limits_{-\infty}^{\infty} \frac{\beta\omega}{1-e^{-\beta\omega}} S(\boldsymbol{q}, \omega)d\omega, \tag{6}$$

where Ω is the solid angle in the wave vector space.

The dynamical structure factor $S(\boldsymbol{q}, \omega)$ can be easily calculated by using the harmonic theory of the lattice dynamics. Writing the ion position vector $\boldsymbol{r}_i(t)$ equal to the equilibrium value $\boldsymbol{r}_i(0)$ plus the displacement $\boldsymbol{u}_i(t)$ and expressing the displacement vector in terms of creation and annihilation operators in the one-phonon approximation with the further assumption that the phones are in thermal equilibrium, $S(\boldsymbol{q}, \omega)$ can be written as

$$S(\boldsymbol{q}, \omega) = \frac{\hbar}{2M} \sum_j \frac{1}{\omega_{\boldsymbol{q}j}} \frac{(\boldsymbol{e}_{\boldsymbol{q}j} \cdot \boldsymbol{q})^2}{(e^{\beta\omega_{\boldsymbol{q}j}}-1)} (\delta(\omega-\omega_{\boldsymbol{q}j})+e^{\beta\omega_{\boldsymbol{q}j}}\delta(\omega+\omega_{\boldsymbol{q}j})), \tag{7}$$

where M is the mass of an atom, $\omega_{\boldsymbol{q}j}$ is the angular frequency of a phonon of wave vector $\boldsymbol{q}$ with polarization index j, and $\boldsymbol{e}_{\boldsymbol{q}j}$ is the polarization vector. Inserting (7) into (6) we obtain

$$S(\boldsymbol{q}) = \frac{\hbar^2}{Mk_{\mathrm{B}}T} \sum_j \frac{(\boldsymbol{e}_{\boldsymbol{q}j} \cdot \boldsymbol{q})^2}{(e^{\beta\omega_{\boldsymbol{q}j}}-1)(1-e^{-\beta\omega_{\boldsymbol{q}j}})}. \tag{8}$$

Equations (1), (5) and (8) show that the basic quantities for investigating the electrical resistivity are the effective pseudopotential matrix element $V(q)$ and the structure factor $S(\boldsymbol{q})$. The structure factor $S(\boldsymbol{q})$ depends solely on the lattice dynamics of the metals. Van Hove [30] has pointed out that $S(\boldsymbol{q}, \omega)$ can be obtained directly from neutron scattering data. However, the present measurements are not in sufficient details to allow the evaluation of the formula (6). In the present work we have used the lattice dynamical model of Sharma and Joshi [17] modified by including angular forces between the ions to evaluate $S(\boldsymbol{q})$ from Eq. (8). The angular forces have been introduced on the lines proposed by de Launay [18] and Clark et al. [19]. Both of these angular forces (known as DAF and CGW models, respectively) are assumed to be significant between first two neighbours only involving two angular force constants. The secular equation determining the angular frequency ω of the normal modes of vibration can be written as

$$|D(\boldsymbol{q})-M\omega^2 I| = 0, \tag{9}$$

where M is the mass of an atom and I is the unit matrix of order three. Each element $D_{ij}(i, j = x, y, z)$ of the dynamical matrix $D(\boldsymbol{q})$ is sum of three contributions due to central, angular and electron-ion interactions. The final expressions for the elements of the dynamical matrix for the de Launay type of angular force (DAF) are obtained as

$$\begin{aligned} D_{ii}(\boldsymbol{q}) &= \tfrac{8}{3}(\alpha_1+2K_1)(1-C_iC_jC_k)+4\alpha_2 S_i^2+4K_2(S_j^2+S_k^2)+4K_e a^3 q_i^2 G^2(qr_0), \\ D_{ij}(\boldsymbol{q}) &= \tfrac{8}{3}(\alpha_1-K_1)S_iS_jC_k+4K_e a^3 q_i q_j G^2(qr_0), \end{aligned} \tag{10}$$

where

$$S_i = \sin(q_i a), \quad C_i = \cos(q_i a) \quad \text{and} \quad G(x) = 3(\sin x - x\cos x)/x^3.$$

In these equations, a is the semi-lattice parameter, q_i is the i-th cartesian component of wave vector $\boldsymbol{q}$, r_0 is the radius of Wigner–Seitz sphere, α_1 and α_2 are the force constants for the first and second neighbour central interactions respectively, K_1 and K_2 are the angular force constants for first and second neighbours respectively, and K_e is the bulk modulus of the electron gas.

The corresponding expressions for elements of the dynamical matrix on the angular force of Clark et al. (CGW) are given by

$$D_{ii}(q) = 8(\alpha_1+2\gamma_1+3\gamma_2)(1-C_iC_jC_k)$$
$$+4\alpha_2S_i^2-4\gamma_1(S_j^2+S_k^2-4S_i^2)+6\gamma_2(S_j^2+S_k^2)+4K_ea^3q_i^2G^2(qr_0),$$
$$D_{ij}(q) = 8(\alpha_1-\gamma_1+\tfrac{3}{2}\gamma_2)S_iS_jC_k+4K_ea^3q_iq_jG^2(qr_0), \tag{11}$$

where γ_1 and γ_2 are the angular force constants corresponding to the nearest and next nearest neighbour interactions respectively for the CGW type of angular forces.

3. *Pseudopotential models*

In recent years, considerable effort has been devoted to establishing the effective potential to represent electron-ion interaction in metals either from first principles or on a pseudopotential concept. Detailed knowledge of this quantity is essential for the determination of fundamental properties of metals, including, for example, band structure, Fermi surface, transport and equilibrium properties. Several authors have developed various kinds of pseudopotentials to fit the experimental data for different physical quantities of the solids. A good account of the pseudopotential formalism and its application to metallic properties is now available in a number of review articles [31, 32] and in Harrison's book [8]. Here we outline the salient features of various pseudopotential models relevant to the present study.

Bardeen [2] was the first to use a primitive form of pseudopotential in the study of electron-phonon interaction in metals. Around each bare ion, he draw a Wigner–Seitz sphere of radius r_s, outside of which he took the field to be Coulombic and inside the sphere he replaced the Hartree–Fock field by a square well of depth U_0. The most extensive calculations of the electron-ion pseudopotential expressed in the model form from first principles have been described by Heine and Abarenkov [20] using observed spectroscopic data pertinent to free atom. These authors assumed an angular momentum dependent model potential for the bare ion, consisting of a square well up to a suitably chosen radius R_M and the Coulomb potential beyond it. Animalu [33], and Animalu and Heine [34] have been modified the original model potential of Heine and Abarenkov by introducing non-local screening of electrons and orthogonalization holes. In another modification, Shaw [21] has reformulated the Heine and Abarenkov model potential is an internally consistent manner by taking into account both the nonlocality and the energy dependence of the potential in the Hartree approximation. Recently Shyu et al. [22] have constructed pseudopotential form factors for simple metals from Shaw's nonlocal model potential by including exchange and correlation effects and have studied a number of metallic properties. Bortolani and Calandra [23] have worked out the electron-ion scattering form factors of heavy alkali metals by taking into account the effects due to the d excited bands in the Heine–Abarenkov model potential. Giuliano and Ruggeri [24] have recently proposed a new form factor of atomic model potential by fitting the parameters from the spectroscopic data of free alkali metals. This model potential has some advantages over that of Heine–Abarenkov due to the absence of discontinuities and the correct behaviour at large distance as well as near the nucleus. Lee and Heine [25] have obtained the APW pseudopotential form factors to represent the electron-ion interaction in alkali metals by phase shift analysis of the Fermi surface data. Schneider and Stoll [26] have obtained the bare-ion potential for a simple metal by fitting the neutron data to his calculated dispersion curves. Recently Sharma and Srivastava [28] have proposed a parametrized expression for the electron-ion interaction potential in simple metals. This model involves a single adjustable parameter and represents in some way improvement over that proposed by Ashcroft [27] who has also used similar arguments but his expression corresponds to an empty core potential for $r < r_c$, where r_c is a parameter measuring the size of the ionic core in a metal.

4. Numerical computations

We have carried out calculations of ideal electrical resistivity of alkali metals (Li, Na, K, Rb, Cs) at different temperatures from Eqs. (1), (5) and (8). The pseudopotential form factors $V(q)$ for these metals are taken from the model potentials of Bardeen [2], Schneider and Stoll [26], Ashcroft [27], Sharma and Srivastava [28], Heine and Abarenkov [20], Shaw [21], Shyu et al. [22], Bortolani and Calandra [23], Giuliano and Ruggeri [24] and Lee and Heine [25]. The structure factor $S(q)$ is determined from Eq. (8) using both forms (DAF and CGW) of modified Sharma and Joshi's model for phonon frequencies and polarization vectors. The integration over q in Eq. (5) was performed numerically and the angular integration was done by using a modification of Houston's spherical six-term integration procedure as elaborated by Betts et al. [35]. If $f(\theta, \phi)$ is any function which is invariant under the operations of the cubic symmetry group and f_A is the value of $f(\theta, \phi)$ for a given direction specified by A, then the Betts et al. six-direction approximation is as follows:

$$\int f(\theta, \phi) d\Omega = \frac{4\pi}{1081080} [117603 f_A + 76544 f_B + 17496 f_C + 381250 f_D + 311040 f_E + 177147 f_F], \tag{12}$$

where the letters A, B, C, D, E and F represent the six directions [100], [110], [111], [210], [211] and [221], respectively. The force constants ($\alpha_1, \alpha_2, K_1, K$, or γ_1, γ_2) and the electronic parameter K_e of the DAF and CGW models are determined by two different methods. In the first method, they are calculated in terms of three elastic constants (C_{11}, C_{12}, C_{44}) and two experimentally known zone boundary phonon frequencies, viz., ν_L (100) and $\nu_T(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, one longitudinal and other transverse in the [100] and [111] directions respectively. The value of K_e so obtained is called experimental K_e. In the second method, the bulk modulus of the electron gas is calculated quantum mechanically using the theoretical expression of Overton [36]. This value of K_e is referred to as theoretical K_e. The remaining four force constants are evaluated in terms of three elastic constants using the long wave limit and the experimental value of phonon frequency ν_T (100) of the transverse branch at the zone boundary in the [100] direction. The values of the zone boundary frequencies were obtained from recent neutron scattering experiments except for caesium for which theoretical values are used. The elastic constants and other relevant parameters used in the present calculation are recorded in Table I.

TABLE I

Constants for alkali metals

Metal	Elastic constants (10^{11} dyn/cm^2)			Ref.	Lattice parameter (Å)	Temp.* (K)	Phonon frequencies (10^{12} Hz)		Ref.
	C_{11}	C_{12}	C_{44}				$\nu_L(100)$	$\nu_T(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	
Lithium	1.481	1.248	1.077	[a]	3.482	78	8.820	7.22	[f]
Sodium	0.808	0.664	0.586	[b]	4.24	90	3.58	2.88	[g]
Potassium	0.416	0.341	0.286	[c]	5.226	4.2	2.21	1.78	[h]
Rubidium	0.314	0.264	0.189	[d]	5.617	110	1.32	1.10	[i]
Caesium	0.261	0.215	0.160	[e]	6.044	4.2	1.008	0.868	[j]

* Temperature to which elastic constants refer.

[a] H. C. Nash, C. S. Smith, *J. Phys. Chem. Solids* **9**, 113 (1959).

[b] W. B. Daniels, *Phys. Rev.* **119**, 1246 (1960); S. L. Quimby, S. Siegel, *Phys. Rev.* **54**, 293 (1938).

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[e] F. J. Kollarits, J. Trivisonno, *J. Phys. Chem. Solids* **29**, 2133 (1968).

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

[i] J. R. D. Copley, B. N. Brockhouse, *Can. J. Phys.* **51**, 657 (1973).

[j] A. O. E. Animalu, F. Bonsignori, V. Bortolani, *Nuovo Cimento* **44**, 159 (1966); based on Heine-Abarenkov model potential calculation.

5. *Results and discussion*

Figures 1—5 show the calculated values of the electrical resistivities of the five alkali metals as a function of temperature together with available experimental data. It will be seen that the results change with the phonon spectrum and the pseudopotential form factors. For experimental as well as theoretical K_e respectively, the DAF and CGW models give exactly similar results and are therefore not shown separately in these figures. The sources of experimental resistivity values plotted in these figures are summarized in Table II. Most earlier measurements on electrical resistivity have been ignored as they are less detailed and unsatisfactory and show several anomalies in the temperature variation of the resistivities (cf. MacDonald [37]), not confirmed by later workers. They do not allow a detailed analysis of ideal electrical resistivity over a continuous temperature range because of insufficient measurements and lack of purity of specimen. Except for sodium, there are not many measurements on the electrical resistivity of alkali metals.

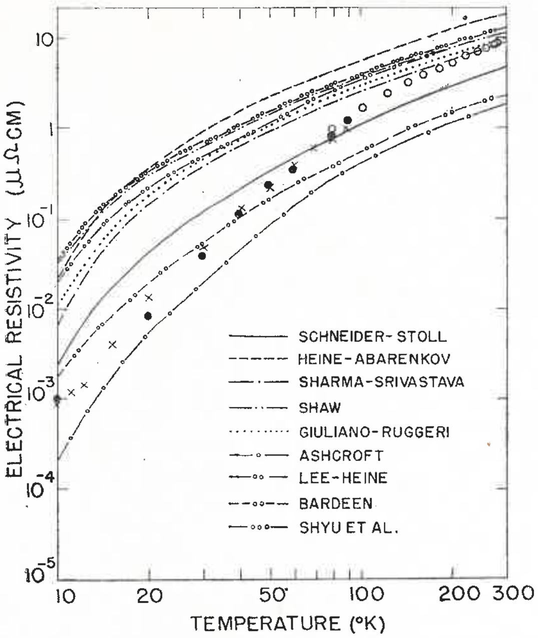

Fig. 1a. **The ideal** electrical resistivity versus temperature for lithium with experimental value of K_e. **Experimental** points: ○ Dugdale and Gugan, ● Rosenberg, × MacDonald et al.

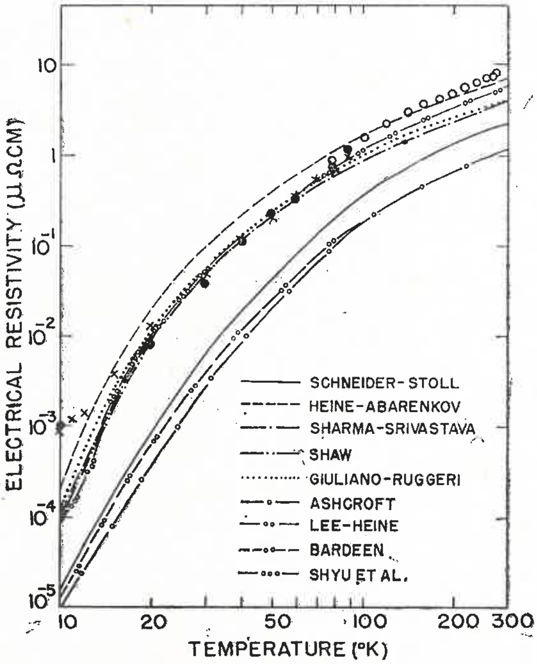

Fig. 1b. **The ideal** electrical resistivity against temperature for lithium with theoretical value of K_e. **Experimental** points: ○ Dugdale and Gugan, ● Rosenberg, × MacDonald et al.

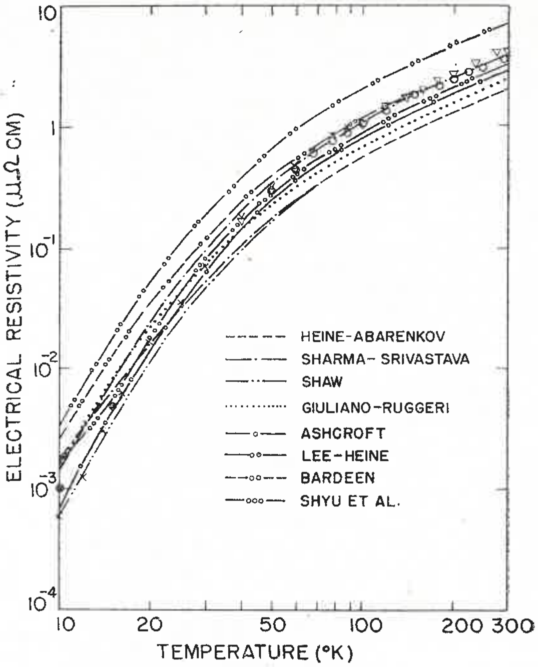

Fig. 2a. The ideal electrical resistivity versus temperature for sodium with **experimental value of K_e.** Experimental points: ○ Dugdale and Gugan, ● MacDonald et al., × Berman **and MacDonald;** ∇ Cook et al.

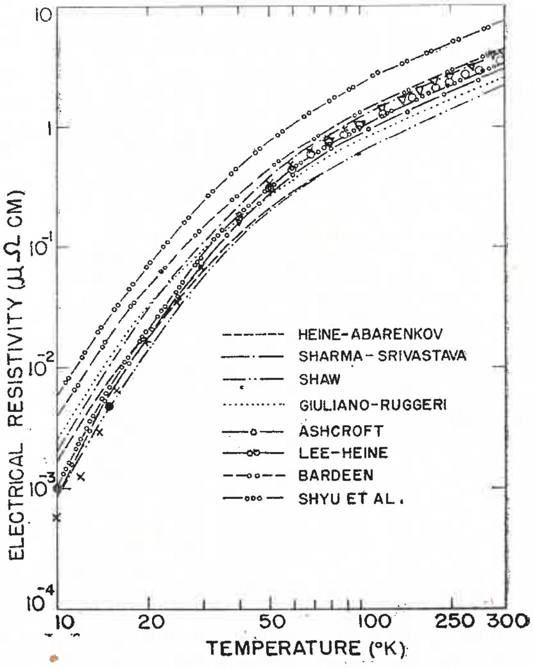

Fig. 2b. The ideal electrical resistivity against temperature for sodium with theoretical value of K_e. Experimental points: ○ Dugdale and Gugan; ● MacDonald et al., × Berman and **MacDonald**, ∇ Cook et al.

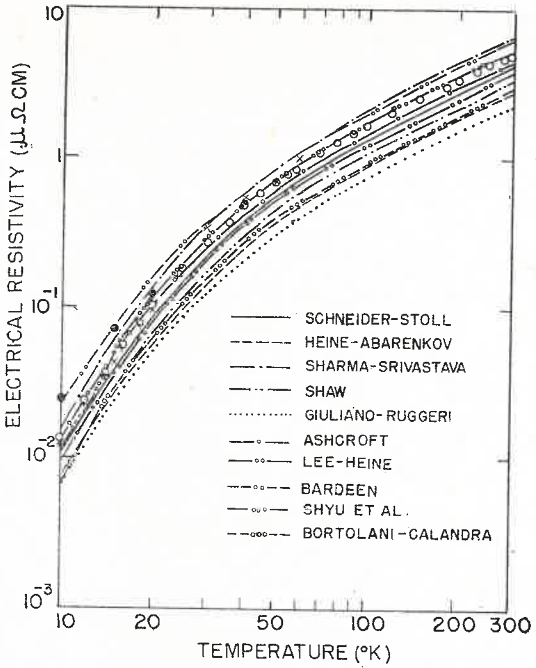

Fig. 3a. The ideal electrical resistivity versus temperature for rubidium with experimental value of K_e. Experimental points: ○ Dugdale and Gugan, ● Natale and Rudnick, × MacDonald et al., + Ekin and Maxfield

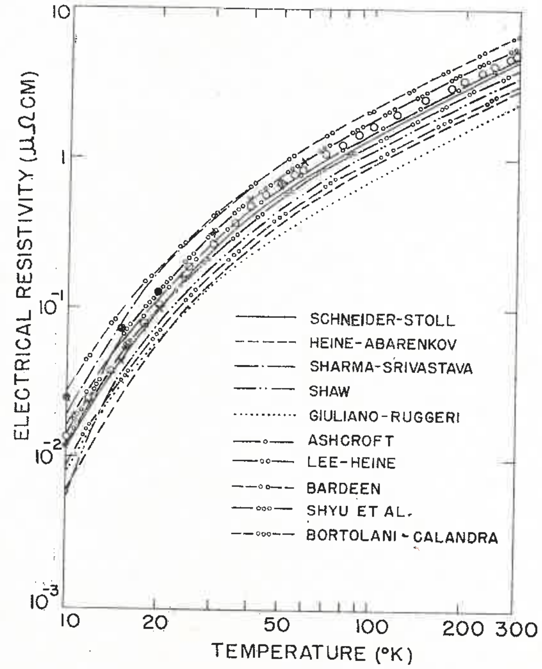

Fig. 3b. The ideal electrical resistivity against temperature for potassium with theoretical value of K_e. Experimental points: ○ Dugdale and Gugan, ● Natale and Rudnick, × MacDonald et al., + Ekin and Maxfield

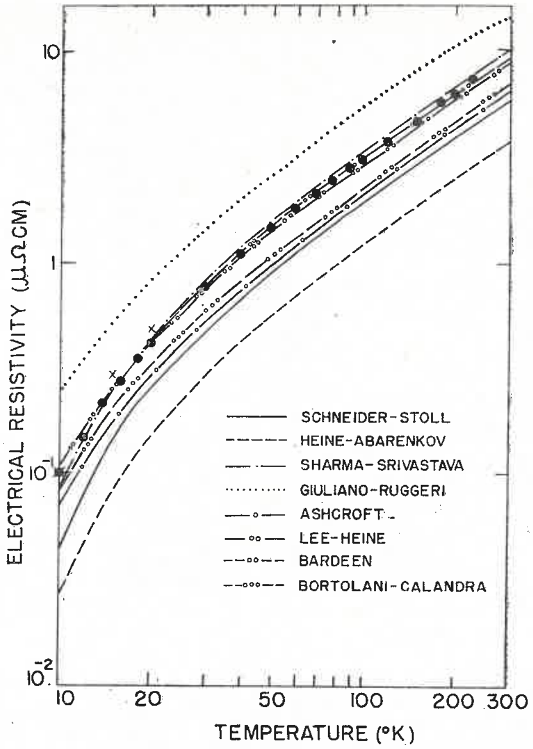

Fig. 4a. The ideal electrical resistivity versus temperature for rubidium with experimental value of K_e. Experimental points: ● Dugdale and Phillips, × MacDonald et al.

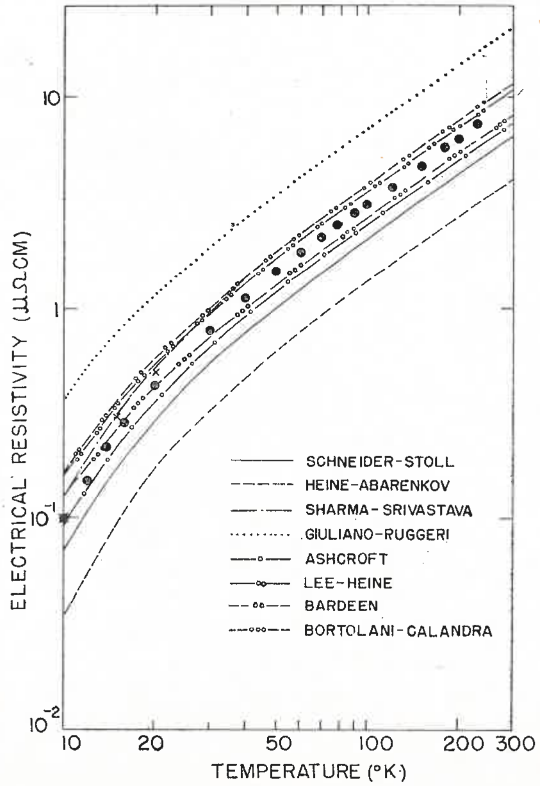

Fig. 4b. The ideal electrical resistivity against temperature for rubidium with theoretical value of K_e. Experimental points: ● Dugdale and Phillips, × MacDonald et al.

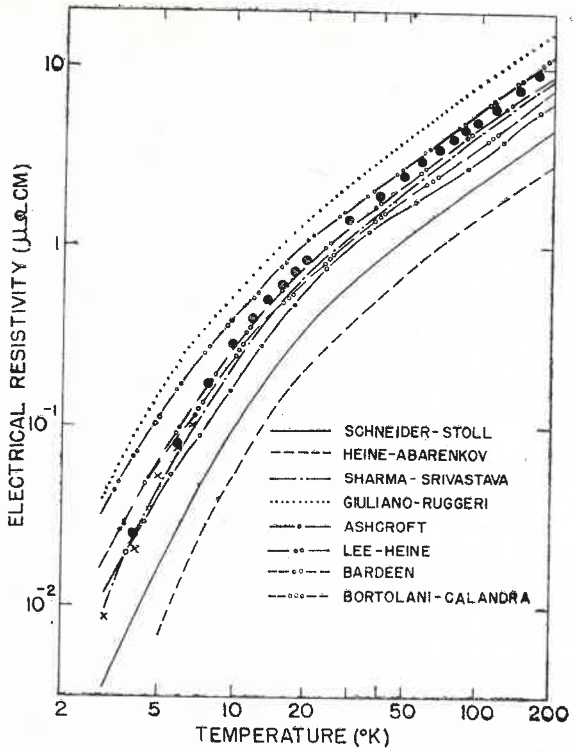

Fig. 5a. The ideal electrical resistivity versus temperature for caesium with experimental value of K_e. Experimental points: ● Dugdale and Phillips, × MacDonald et al.

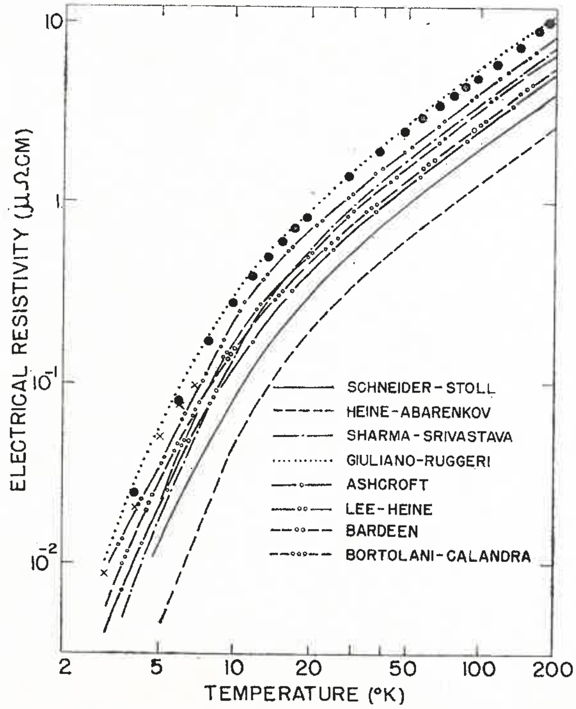

Fig. 5b. The ideal electrical resistivity against temperature for caesium with theoretical value of K_e. Experimental points: ● Dugdale and Phillips, × MacDonald et al.

TABLE II

Temperature ranges for the experimental electrical resistivity data for alkali metals

Metal	Temperature range (K)	Source
Lithium	10—90	[a]
	11—90	[b]
	80—290	[c]
Sodium	3.2—15	[b]
	4—90	[d]
	40—360	[e]
	50—295	[c]
Potassium	1—25	[f]
	2.5—20	[g]
	3.5—60	[b]
	8—295	[c]
Rubidium	2—300	[h]
	2.6—20	[b]
Caesium	2—7	[b]
	2—300	[h]

[a] H. M. Rosenberg, *Phil. Mag.* **1**, 738 (1956).
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[e] J. G. Cook, M. P. van der Meer, M. K. Laubitz, *Can. J. Phys.* **50**, 1386 (1972).
[f] J. W. Ekin, B. W. Maxfield, *Phys. Rev.* **B4**, 4215 (1971).
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The most comprehensive work on the electrical resistivities of alkali metals at low temperature down to 2 K is that of MacDonald et al. [38], but their results for lithium and sodium refer to two-phase mixtures of unknown proportions. The most accurate work on the ideal electrical resistivity of alkali metals in the temperature range 2—300 K has been reported by Dugdale and Gugan [39], and Dugdale and Phillips [40]. Recently, Cook et al. [41] have presented reliable electrical data for pure free sample of sodium from 40 to 360 K.

It will be noticed from Figs. 1—5 that our calculated resistivity curves are in reasonably good agreement with experiments except for lithium at low temperatures. However, in lithium the significance of experimental data at low temperatures is rather doubtful due to martensitic transformation [42] occurring around 80 K. Similar phase transformation [43] also occurs in sodium below about 40 K. An overall study of Figs. 1—5 indicates that for lithium calculations using Giuliano and Ruggeri, and Sharma and Srivastava form factors in the DAF and CGW models with experimental K_e agree better with observations at high temperatures, while Bardeen potential provides better agreement in the low temperature region. For theoretical K_e in DAF and CGW models, better agreement with experiments in obtained for Heine and Abarenkov, and Sharma and Srivastava model potentials in the high and intermediate temperature ranges, respectively. In the case of sodium and potassium, calculations based on Shyu et al. potential lie closer to the experiments for both models. For rubidium, the agreement between theory and experiment is reasonably good with Lee and Heine and Bortolani and Calandra potentials for experimental K_e, while Sharma and Srivastava, Lee and Heine, and Bardeen potentials give very good results for theoretical K_e. In caesium, the form factors of Bardeen is found to give somewhat better results for both models with experimental K_e, whereas Giuliano and Ruggeri potential calculations lie very close to the experiments for theoretical K_e. In general experimental K_e in either of model gives higher values of the electrical resistivity as compared to the theoretical K_e throughout the whole temperature range for all alkali metals. The difference between the results on the two values of K_e is maximum for lithium. On the whole there seems to be satisfactory agreement between theory and experimental data.

The discrepancies between theory and experiments at higher temperatures can be attributed to the neglect of various anharmonic contributions. In the present work, we have not incorporated the temperature variation of elastic constants. This may turn out to be an important effect because the elastic constants of metals show a marked variation with temperature. At higher temperatures multiphonon processes begin to operate and the one-phonon approximation on which the formula (8) is obtained becomes less valid. Also the phonons vary with temperature and develop finite lifetime which should be included in the theory. One should also take into account the small change in the pseudopotential brought about by volume changes through the thermal expansion. Although these effects are small, they are likely to introduce relatively important changes in the magnitude of resistivity which depends very sensitively on the shape of phonon spectrum and form factors. However, it does not seem possible to do a complete calculation taking into account all the conceivable corrections to the theory.

For lithium and sodium at low temperatures, a phase transformation [42, 43] of martensitic type occurs which produces a mixture of faulted hcp phase when the sample is cooled below about 78 K and 37 K respectively. This transformation makes the interpretation of the experimental data somewhat complicated below this temperature. Since the electrical resistivity depends upon the phonon spectrum sensitively at low temperature, the discrepancies for lithium and sodium may be partly attributed to change in crystal structure and hence in the phonon spectrum due to martensitic transformation.

It emerges from the present study that the ideal resistivity deduced from Ziman–Baym formula with modified Sharma and Joshi's model for the phonon spectrum agrees reasonably well with experiments. This proves the adequacy of Ziman–Baym formulation. The results further show that the magnitude of electrical resistivity is very sensitive to the form factors of electron-ion pseudopotential. With appropriate selection of pseudopotential it is possible to get very good agreement with experiments.

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