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IDEAL THERMAL RESISTIVITY AND LORENTZ NUMBER OF ALKALI METALS

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The ideal thermal resistivity and Lorentz number of alkali metals due to scattering of conduction electrons by thermal vibrations are determined at different temperatures from various available pseudopotential form-factors for electron-ion interaction. Information about the dynamical structure factor is obtained through the phonon spectrum derived from a modification of Sharma and Joshi's lattice dynamical model by introducing de Launay and CGW type of angular forces between the ions. The calculated temperature variation of the thermal resistivity shows reasonably good agreement with experiments, except for lithium and sodium in the low temperature range. The Lorentz number curves show marked variation with temperature in sharp departure to Wiedemann–Franz law.

1. *Introduction*

In pure metals, the resistance to the transport of heat is mainly due to the scattering of conduction electrons by the thermal vibrations of the lattice. Ziman [1] and Baym [2] have given general formulation of the problem from a variational solution of the Boltzmann transport equation. Any theoretical study of phonon limited ideal thermal resistivity by this approach requires a knowledge of two main elements, namely, the electron-phonon matrix element and the dynamical structure factor of the ion system. For reliable results, these two quantities should be known in sufficient details.

During the past few years, the pseudopotential theory of metals [3] has proved to be an elegant theoretical framework for the evaluation of form-factors of electron-phonon interaction in simple metals. Several authors have proposed different forms of pseudopotentials from empirical and semi-empirical considerations by fitting the parameters to some experimental data such as atomic energy levels, liquid resistivity or phonon dispersion curves [4]. Attempt has also been made to calculate the pseudopotential from first principles [3]. The subject has been reviewed by Cohen and Heine [5] and they have summarized the pseudopotentials which have been developed for a large number of metals.

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In this paper, we report a theoretical study of temperature variation of ideal thermal resistivity of alkali metals using various available model pseudopotentials [6–15] for electron-ion coupling. The dynamical structure factor needed in the calculation is obtained from the phonon dispersion curves deduced from modified Sharma and Joshi's model [16] which incorporates angular interactions between the ions on the lines suggested by de Launay [17] and Clark et al. [18]. Formidable angular integrations are carried out by a modified Houston's six-term interpolation procedure [19]. Also included are the computations of the Lorentz number for these metals using the electrical resistivity values reported in an earlier work [20]. The results of calculations are compared with available experimental information.

2. *Theory*

The ideal thermal resistivity represents the resistance to the flow of heat due to the scattering of conduction electrons by the thermal vibrations. Baym [2] has derived a variational expression for the ideal resistivity W_i due to lattice vibration scattering. In the weak coupling approximation, for cubic metals it may be written as

$$W_i = \frac{1}{L_0 T} \frac{m}{nZe^2} \tau_t^{-1}, \tag{1}$$

where $L_0 = \pi^2 k_B^2/3e^2$. Here k_B is the Boltzmann constant, m—the mass of an electron, e—the electronic charge, n—the number of ions per unit volume, Z—the valency of the metal and τ_t is the relaxation time for the scattering of electrons by thermal vibration given by

$$\tau_t^{-1} = \frac{3\pi}{2\hbar m k_F^2 S_F^2} \iint \frac{dS_k}{v_k} \frac{dS_{k'}}{v_{k'}} |\langle \boldsymbol{k}'|V|\boldsymbol{k}\rangle|^2$$

$$\times \int_{-\infty}^{\infty} \frac{\beta\omega}{1-e^{-\beta\omega}} S(\boldsymbol{q}, \omega)\left(\boldsymbol{q}^2 - \frac{1}{2\pi^2}(\beta\omega)^2\boldsymbol{q}^2 + \frac{3k_F^2}{\pi^2}(\beta\omega)^2\right) d\omega, \tag{2}$$

where $\beta = \hbar/k_B T$ and $\boldsymbol{q} = \boldsymbol{k}'-\boldsymbol{k}$. In this expression, $\boldsymbol{k}$ and $\boldsymbol{k}'$ are the wave vectors of the electron in the initial and final states, v_k — the velocity of electron with wave vector $\boldsymbol{k}$, k_F — the Fermi wave vector, S_F — the area of the Fermi surface, $\langle \boldsymbol{k}'|V|\boldsymbol{k}\rangle$ is the matrix element of screened pseudopotential representing the scattering of an electron from state $\boldsymbol{k}$ to state $\boldsymbol{k}'$ on the Fermi surface with the absorption of a phonon of frequency ω, and $S(\boldsymbol{q}, \omega)$ is the dynamical structure factor of the ion system.

For a spherical geometry of the conduction band, the two surface integrals in Eq. (2) can be reduced to a three-dimensional integral over $\boldsymbol{q}$ so that the above equation becomes

$$\tau_t^{-1} = \frac{3}{16\hbar m v_F^2 k_F^4} \int_0^{2k_F} S'(\boldsymbol{q})\, |V(q)|^2 q\, dq\, d\Omega, \tag{3}$$

where

$$S'(\boldsymbol{q}) = \int\limits_{-\infty}^{\infty} \frac{\beta\omega}{1-e^{-\beta\omega}} S(\boldsymbol{q}, \omega) \left(q^2 - \frac{1}{2\pi^2} (\beta\omega)^2 q^2 + \frac{3k_F^2}{\pi^2} (\beta\omega)^2 \right) d\omega, \tag{4}$$

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

In the one-phonon approximation, the dynamical structure factor $S(\boldsymbol{q}, \omega)$ is related to the phonon spectrum through the relation [21]

$$S(\boldsymbol{q}, \omega) = \frac{\hbar}{2M} \sum_j \frac{1}{\omega_{qj}} \frac{(\boldsymbol{e}_{qj} \cdot \boldsymbol{q})^2}{(e^{\beta\omega_{qj}}-1)} [\delta(\omega-\omega_{qj}) + e^{\beta\omega_{qj}} \delta(\omega+\omega_{qj})], \tag{5}$$

where M is the mass of an atom, and ω_{qj} and $\boldsymbol{e}_{qj}$ are the angular frequency and polarization vector of a lattice mode with wave vector $\boldsymbol{q}$ and polarization index j. Use of Eq. (5) into Eq. (4) yields

$$S'(\boldsymbol{q}) = \frac{\hbar^2}{Mk_B T} \sum_j \frac{(\boldsymbol{e}_{qj} \cdot \boldsymbol{q})^2}{(e^{\beta\omega_{qj}}-1)(1-e^{-\beta\omega_{qj}})} \times \left[q^2 - \frac{1}{2\pi^2} (\beta\omega_{qj})^2 q^2 + \frac{3k_F^2}{\pi^2} (\beta\omega_{qj})^2 \right]. \tag{6}$$

3. *Numerical computations*

The computation of the temperature dependence of ideal thermal resistivities of alkali metals (Li, Na, K, Rb, Cs) is made from Eqs. (1), (3) and (6). The integration over q was performed numerically and the angular integration was done by using a modified Houston spherical six-term integration procedure [19]. The six directions of q used in the calculation are: [100], [110], [111], [210], [211] and [221]. The values of effective electron-ion pseudopotential form factors of alkali metals are obtained from model potentials of Bardeen [6], Heine and Abarenkov [7], Schneider and Stoll [8], Ashcroft [9], Shaw [10], Giuliano and Ruggeri [11], Bortolani and Calandra [12], Shyu et al. [13], Lee and Heine [14], and Sharma and Srivastava [15]. The structure factor $S'(q)$ is determined from Eq. (6) using the phonon frequencies and polarization vectors derived from modified Sharma and Joshi's model [16] which takes into account angular interaction between the ions. The angular forces are incorporated on two approaches, one that on de Launay [17] angular force (DAF) model and the other on Clark, Gazis and Wallis [18] (CGW) model. The model described elsewhere [20] involves five parameters, namely, two central force constants (α_1, α_2), two angular force constants (K_1, K_2) and an electronic parameter K_e. These are determined by two different methods. In the first method, they are correlated to the three elastic constants in the long wave limit and two experimentally measured zone boundary frequencies, ν_L (100) and ν_T $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, of the longitudinal and transverse modes travelling in [100] and [111] directions respectively. The value of K_e obtained by this method is referred to as experimental K_e. In the second method, the electronic parameter K_e is determined theoretically using the quantum mechanical expression due to Overton [22]. This value of K_e is called theoretical K_e. The other four parameters are determined by relating them to the three elastic constants and the experimental transverse zone boundary frequency ν_T (100) in the [100] direction. The elastic constants and other relevant parameters fed into the calculations are given in Table I of Ref. [20].

4. Results and discussion

a) Thermal resistivity

The results of the calculation of ideal thermal resistivities of the five alkali metals (Li, Na, K, Rb, Cs) on three model psudopotentials (Lee and Heine [14], Ashcroft [9] and Sharma and Srivastava [15]) are plotted in Figs. 1–5 against temperature on the logarithmic scale together with the available experimental data. The results from other potentials show similar temperature variation and are not shown in these figures. As in earlier studies [20], the DAF and CGW angular forces with experimental K_e give similar results for alkali metals. For the theoretical K_e, the values of resistivities obtained from the two models also do not show difference and hence they are not shown separately in these figures. The sources of the experimental data for thermal resistivities plotted in these

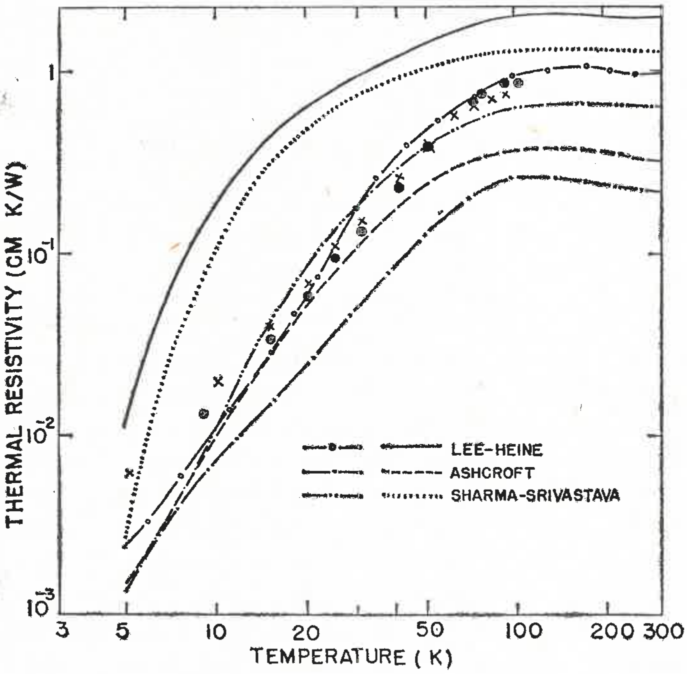

Fig. 1. The ideal thermal resistivity versus temperature for lithium. First set, theoretical K_e; second set, experimental K_e. Experimental points: × Rosenberg; ● MacDonald et al.

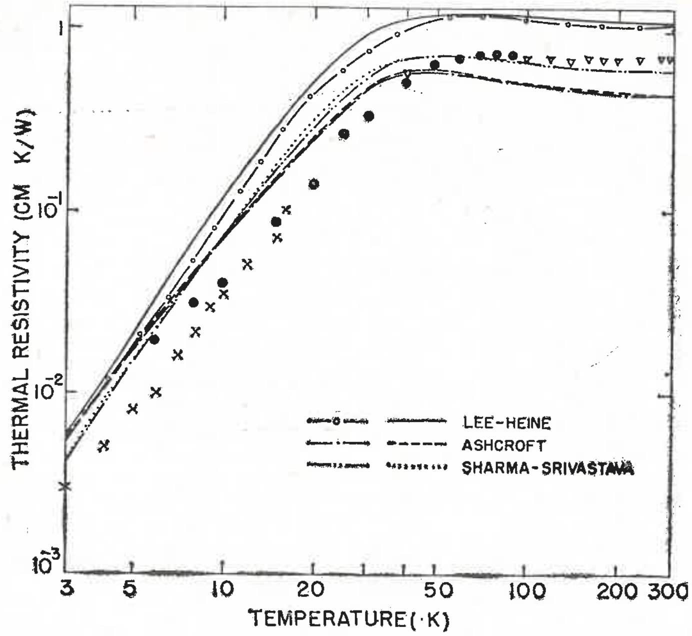

Fig. 2. The ideal thermal resistivity versus temperature for sodium. First set, theoretical K_e; second set, experimental K_e. Experimental points: × MacDonald et al.; ● Barman and MacDonald; ▽ Cook et al.

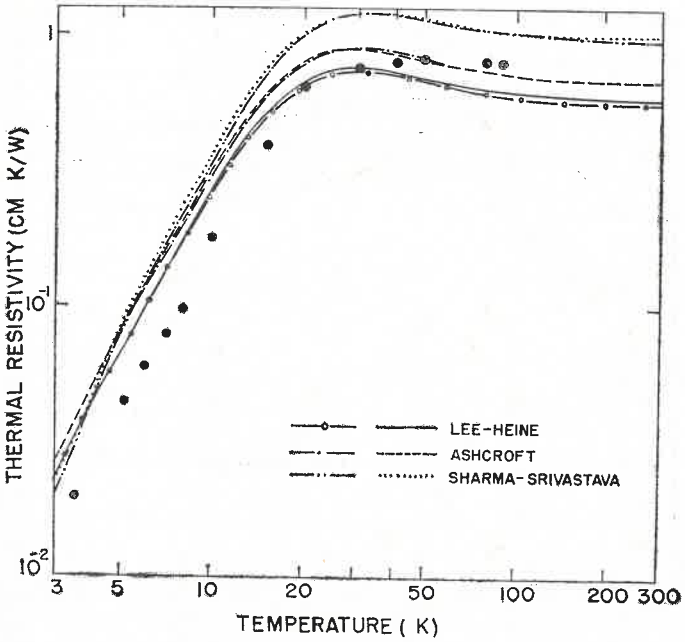

Fig. 3. The ideal thermal resistivity versus temperature for potassium. First set, theoretical K_e; second set, experimental K_e. Experimental points: ● MacDonald et al.

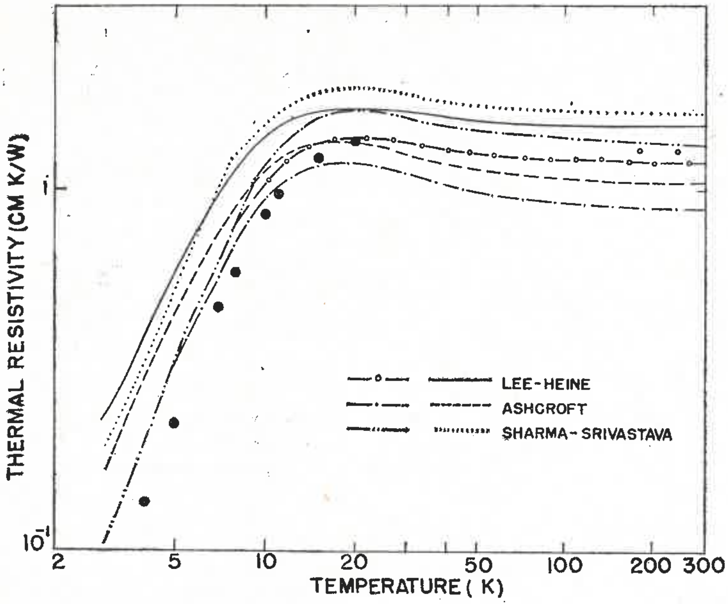

Fig. 4. The ideal thermal resistivity versus temperature for rubidium. First set, theoretical K_e; second set, experimental K_e. Experimental points: ● MacDonald et al.

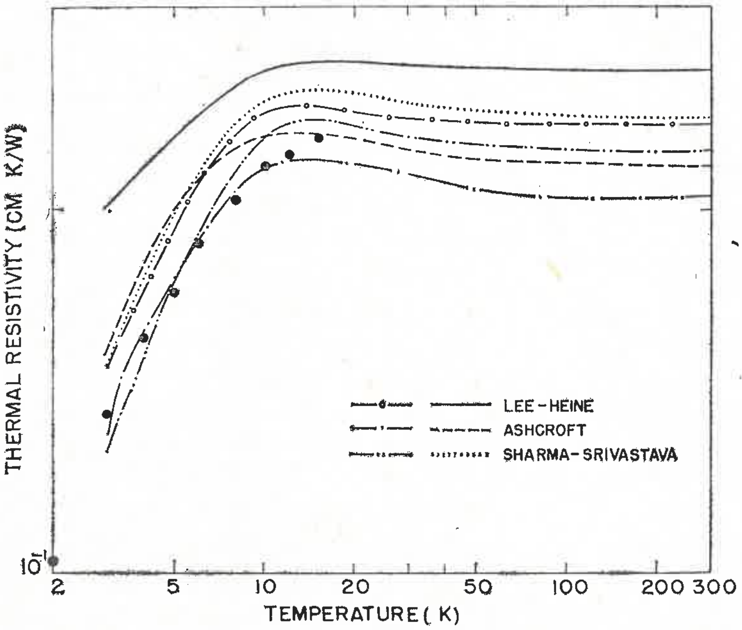

Fig. 5. The ideal thermal resistivity versus temperature for caesium. First set, theoretical K_e; second set, experimental K_e. Experimental points: ● MacDonald et al.

figures are listed in Table I. Except for sodium, there are not many measurements on the thermal resistivity of alkali metals. The most comprehensive measurements on the thermal resistivity of alkali metals in the low temperature range have been reported by MacDonald et al. [23]. However, their data for lithium and sodium refer to two-phase mixtures of unknown proportions. Recently Cook et al. [24] have presented reliable values for the thermal resistivity of high purity sodium over the temperature range 4 to 360 K.

TABLE I

Temperature ranges for the experimental thermal resistivity data for alkali metals

Metal	Temperature range (K)	Source
Lithium	2–90	[a]
	9–100	[b]
Sodium	2.5–16	[b]
	4–90	[c]
	40–260	[d]
Potassium	3.5–90	[b]
Rubidium	2–20	[b]
Caesium	2–15	[b]

[a] H. M. Rosenberg, *Phil. Mag.* **1**, 738 (1956).
[b] D. K. C. MacDonald, G. K. White, S. B. Woods, *Proc. R. Soc.* **A235**, 358 (1956).
[c] R. Berman, D. K. C. MacDonald, *Proc. R. Soc.* **A209**, 368 (1951).
[d] J. G. Cook, M. P. van der Meer, M. J. Laubitz, *Can. J. Phys.* **50**, 1386 (1972).

We notice from Figs. 1–5 that the temperature variation of the theoretical and experimental curves is of similar nature, but they somewhat disagree in the case of lithium and sodium at low temperatures. The disagreement is more pronounced in the case of lithium which can be attributed due to the distortion of the Fermi surface. Further, the experimental data for these metals in the low temperature region are not very reliable due to martensitic phase transformation occurring in them [25, 26]. The experimental data for lithium agree better with the theoretical values deduced from Lee and Heine model potential over a considerable temperature range studied. For sodium, the calculated values of the resistivity are substantially higher than the experimental ones up to about 50 K, while at higher temperatures they show good agreement with experiments for the results obtained from Sharma and Srivastava model potential. For potassium, at low temperatures the resistivity obtained from Giuliano and Ruggeri potential lies closer to the experimental values, while at higher temperatures calculations from Ashcroft, and Schneider and Stoll pseudopotentials give a better fit to the experimental data. In the case of rubidium, Schneider and Stoll form-factors are found to give better agreement with experiments at low temperatures. For caesium, the agreement between theory and experiments is better for

Ashcroft, and Schneider and Stoll model potentials. An overall survey of the thermal resistivity results obtained indicates that the Schneider and Stoll model potential gives better agreement with the observations for potassium, rubidium and caesium, while for lithium and sodium the results from Lee and Heine, and Sharma and Srivastava form factors respectively lie much closer to the experiments.

b) Lorentz number

The temperature variation of the thermal resistivity at low temperatures is different from that of electrical resistivity. This effect is usually represented in terms of the function $L = \varrho_i / W_i T$, known as the Lorentz number. This quantity must be constant for all metals if the conduction electrons were scattered elastically. This condition is expected to be true at higher temperatures.

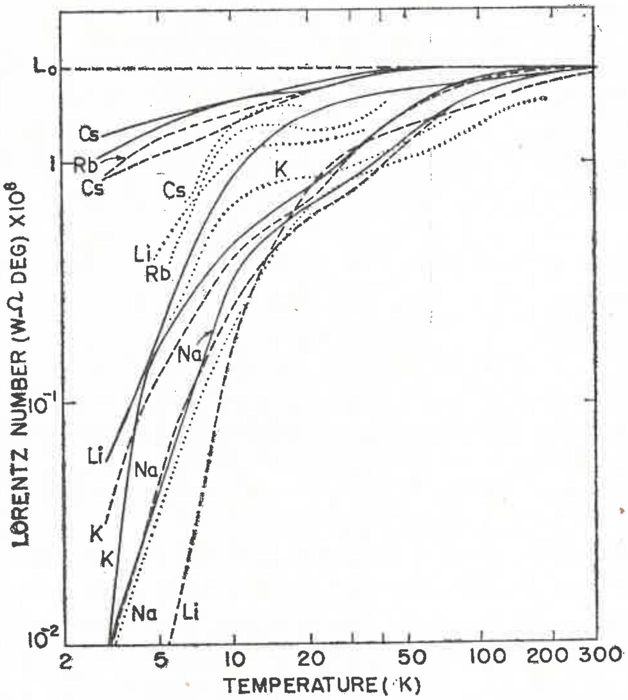

Fig. 6. Temperature variation of the Lorentz number of alkali metals. Full lines experimental K_e; dashed lines, theoretical K_e. Dotted curves show experimental measurements

Using the electrical resistivities calculated in the previous paper [20], the Lorentz number for alkali metals are evaluated. In Figs. 6, we show the results of the calculation of Lorentz number on the basis of Giuliano and Ruggeri model potential together with the values deduced from experimental data on electrical and thermal resistivities. The results from other potentials are similar to those obtained from Giuliano and Ruggeri model potential and are not shown in these figures.

We notice from the figures that the theoretical Lorentz number curves show approximately the same temperature behaviour as has been found experimentally, but at low temperatures the experimental curves seem to fall considerably below the theoretical curves. Maximum disagreement with experiment is found in the case of lithium. Further, the Lorentz number results show marked variation with temperature in sharp contrast to Wiedemann–Franz law. In the intermediate temperature region, the experimental curves show dip and have the tendency to fall below the theoretical values. This may be attributed to the extra thermal resistivity produced by inelastic electron-electron scattering. At higher temperatures where the electron scattering is mostly elastic, the calculated curves tend to reach the Sommerfeld value of 2.443×10^{-8} Watt Ohm $\deg^{-2}$ and the Wiedemann–Franz law is obtained.

The disagreement between theory and experiment can be ascribed to the neglect of various anharmonic effects such as temperature variation of elastic constants, multiphonon processes and change in pseudopotential form factors due to thermal expansion. The present study shows that the thermal resistivity of metals depends more sensitively on the pseudopotential form factors than does the electrical resistivity. As such the errors introduced by various anharmonic effects is expected to be more serious. In lithium [25] and sodium [26] at low temperatures, the situation is further complicated by change of crystal structure due to martensitic transformation below about 80 and 40 K respectively. This transformation causes unusual variations in the elastic and thermal properties and makes doubtful the interpretation of our results based on simple body-centred cubic structure at the lowest temperatures. The electron-electron scattering is another mechanism by which heat transport may be affected but not the charge transfer in metals [27, 28]. It is possible to explain some deviation in magnitude and temperature variation of thermal resistivity in terms of electron-electron scattering.

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