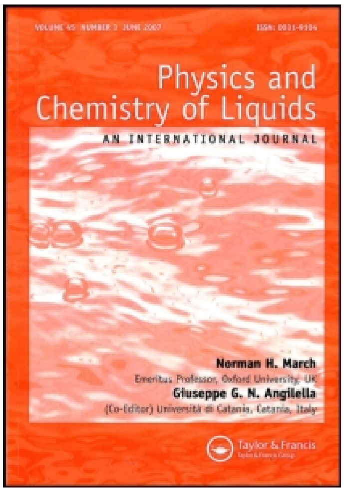

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Temperature Dependence of Transport Properties of Liquid Sodium and Potassium

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TEMPERATURE DEPENDENCE OF TRANSPORT PROPERTIES OF LIQUID SODIUM AND POTASSIUM

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The electrical and thermal resistivities of liquid Na and K are calculated over a range of temperature at and above the melting point using the solutions of the Boltzmann equation, the form factors constructed using the Dagens–Rasolt–Taylor (DRT) model potential, the screening function of Geldart and Taylor and the X-ray structure factors of Waseda. The ratio of the electrical and the thermal resistivities is compared with the Wiedemann–Franz law and with experiment. We show that the deviation from the Lorenz number can be explained by the inelastic part of the electron–phonon scattering and the electron–electron scattering.

Keywords: Liquid metal; Sodium; Potassium; Electrical resistivity; Thermal conductivity; Lorenz number

I. INTRODUCTION

Since the Ziman [1,2] formula for static electrical resistivity was introduced, many calculations have been done on liquid metals. Most of the work was done at the melting point only and many early results disagreed due to the use of inaccurate structure factors or inadequate pseudopotentials. Despite the fact that now we have accurate measurements of the structure factors and model potentials which describe the properties of liquid metals well, calculations of electrical resistivity at temperatures higher than the melting point

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have lagged behind and very few attempts have been made to calculate thermal conductivities. The goal of the current study is the calculation of these two transport properties of liquid sodium and potassium over a range of temperatures at and above the melting point. We use the Ziman formula to calculate electrical resistivity and the Ziman-like formula (including the electron–phonon inelastic scattering) to calculate the thermal conductivity. The model potential of Dagens–Rasolt–Taylor [3,4] is used to derive the form factors. By calculating both the electrical and the thermal resistivities at the same temperatures we are able to calculate their ratio and compare it with the Wiedemann–Franz law and with experiment.

II. The Ziman Formula

The Ziman formula [1,2] for static electrical resistivity is derived in the nearly-free-electron model by using the first Born approximation in the linearized Boltzmann equation. The resulting expression for resistivity is:

$$\rho = \frac{3\pi\Omega_0 m_e^2}{4e^2\hbar^3 k_\mathrm{f}^6}\int_0^{2k_F} \left|W(q)\right|^2 S(q) q^3 dq, \tag{1}$$

where k_f is the Fermi wave vector, Ω_0 is the ionic volume, e and m_e are the electron charge and mass, respectively. The two important components of the formula are the structure factor $S(q)$, which can be obtained from X-ray or neutron diffraction, and the form factor $W(q)$ (also called the screened electron-ion matrix element), which can be derived based on a model potential.

The thermal resistivity similarly results from the Boltzmann equation and is given by [5,6]

$$\begin{aligned}\lambda = \frac{3\pi\Omega_0 m_e^2}{4e^2\hbar^3 k_\mathrm{f}^6}\frac{1}{L_0 T}\Bigg[\int_0^{2k_f} & |W(q)|^2 q^3 S(q)\, dq \\ & + \frac{3\hbar^2 k_\mathrm{f}^2}{2Mk_\mathrm{B}T\pi^2}\int_0^{2k_\mathrm{f}} |W(q)|^2 q^3 S(q)\, dq \\ & - \frac{\hbar^2 k_\mathrm{f}^{2-}}{Mk_\mathrm{B}T\pi^2}\int_0^{2k_\mathrm{f}} \left|W(q)\right|^2 q^5 S(q)\, dq\Bigg],\end{aligned} \tag{2}$$

where M is the atomic mass and k_B the Boltzmann constant.

Note that if the second and third terms, which represent the electron–phonon inelastic scattering, are neglected, we obtain the well-known Wiedemann–Franz law, which includes only the elastic scattering:

$$\frac{\rho}{\lambda} = L_0 T, \tag{3}$$

where T is the Kelvin temperature, and the Lorenz number $L_0 = \pi^2/3(k_B/e)^2 = 2.45 \times 10^{-8}\,\mathrm{W\,\Omega/K^2}$.

III. The Form Factor

The form factors needed for the use of the Ziman formula are obtained as follows. First, the bare electron–ion interaction is calculated based on the DRT model potential [3,4] and following the procedure given by Shukla and Taylor [7,8]; these calculations require only the knowledge of the ionic volume and the parameters of the model potential [4]. Second, the exchange and correlation effects of the electron gas are accounted for by the use of the screening function of Geldart and Taylor [9,10]. Finally, we calculate the screened form factor to be used in Eqs. (1) and (2) using the results of Rasolt [3]. We would like to emphasize that the model potential used has no adjustable parameters and is derived from first principles.

IV. Application to Sodium and Potassium

The temperatures and the corresponding ionic volumes used in the current calculations are given in Table I.

TABLE I Ionic volumes

Na		*K*	
T (°C)	Ω_0 (a.u.)^3	T (°C)	Ω_0 (a.u.)^3
105	278.89	70	527.19
200	284.69	105	543.45
300	294.74	200	548.62
450	303.99	350	571.85
550	312.42	450	591.92

TABLE II Calculated and experimental electrical resistivities and thermal conductivities

Na					
T (°C)	105	200	300	450	550
$\rho_{\mathrm{calc.}}(10^{-8}\,\Omega\,\mathrm{m})$	9.99	12.63	16.7	24.11	31.56
$\rho_{\mathrm{exp.}}(10^{-8}\,\Omega\,\mathrm{m})$	9.83	13.45	17.35	24.56	30.20
% Error	2	6	5	4	4
$\kappa_{\mathrm{calc.}}(\mathrm{W\,m\,K^{-1}})$	91.48	90.73	83.23	70.48	63.37
$\kappa_{\mathrm{exp.}}(\mathrm{W\,m\,K^{-1}})$	90.2	81.67	67.31	67.31	62.28
% Error	2	10	10	5	2
K					
T (°C)	70	105	200	350	450
$\rho_{\mathrm{calc.}}(10^{-8}\,\Omega\,\mathrm{m})$	14.72	16.42	22.55	32.14	42.90
$\rho_{\mathrm{exp.}}(10^{-8}\,\Omega\,\mathrm{m})$	13.65	15.75	20.99	31.32	39.50
% Error	7	4	7	6	6
$\kappa_{\mathrm{calc.}}(\mathrm{W\,m\,K^{-1}})$	56.3	52.64	50.84	45.64	40.94
$\kappa_{\mathrm{exp.}}(\mathrm{W\,m\,K^{-1}})$	57.62	55.43	50.63	44.10	40.10
% Error	2	5	1	3	2

After the form factor is calculated by following the steps in Section III, the X-ray measurements of the structure factor of Waseda [11] are used in the integration in Eqs. (1) and (2). The results are presented in Table II and compared to the experimental measurements [12].

V. Thermal Conductivity and Lorenz Ratio

Cook and Fritsch measured the electrical and thermal conductivity simultaneously for alkali metals [13–15]. These measurements showed that the thermal conductivity differs from the value obtained by the application of Wiedemann–Franz law. Based on their measurements and other theoretical considerations, they showed that contributions from the ionic conductivity and the inelastic scattering are small and of opposite sign so that they cancel. However, they suggested a correction to the Wiedemann–Franz law for second-order effects in the Lorenz function (i.e. off-diagonal matrix elements) similar to the work of Laubitz [16], which is given by [17,18]

$$\kappa = \frac{(L_0 - S^2)T}{\rho} \tag{4}$$

where S is the thermoelectric power and ρ is the electrical resistivity.

The electron–electron scattering contribution to the thermal resistivity is a linear function of temperature given by

$$W_{ee} = BT \tag{5}$$

where B can be measured experimentally. Thus Cook and Fritsch suggested a formula for thermal conductivity given by

$$\kappa = \left[W_{ee} + \frac{\rho}{(L_0 - S^2)T} \right]^{-1} \tag{6}$$

where W_{ee} is the contribution due to electron–electron scattering, S is the thermoelectric power and ρ is the electrical resistivity. MacDonald and Geldart [19] have calculated the electron–electron scattering contribution to the thermal conductivity of solid simple metals using an approximation to the scattering function based on the Landau Fermi liquid theory, and a similar calculation has been done by Lundmark [20]. The calculation of the thermal conductivity using the Eq. (6) requires the knowledge of the electrical conductivity as a function of temperature, the thermoelectric power as a function of temperature and the contribution due to electron–electron scattering.

In our calculations we used Eq. (2), which includes the inelastic electron–phonon part. As we can see in Table III, if we calculate from our results the ratio of electrical and thermal resistivities, we get a small negative correction to the theoretical value of the Lorenz number. This correction does not, however, account entirely for the deviation from the experimental measurements, as shown in the first column of Table III. If we include the contribution of the electron–electron scattering to the thermal resistivity as calculated by MacDonald and Taylor, we can account fully for the deviation from the theoretical Lorenz number as shown in Table III.

TABLE III Calculated and measured ratio $\rho/\lambda T$ (10^{-8} W Ω/K^2)

Calculated using Eq. (2)	*Calculated including* W_{ee}	*Experimental*
2.41	2.37	2.37
2.41	2.31	2.31

VI. DISCUSSION AND CONCLUSION

The calculated electrical resistivities are in very good agreement with the experimental results. At all temperatures the deviation from experiment is less than 6%, which is comparable to other work done at the melting points using the Ziman formula [21–23]. However, we obtained better agreement at temperatures above the melting point for sodium and potassium than did the work of Sinha *et al.* [24]. These authors used the optimized model potential of Shaw [25], the Vashishta–Singwi [26] screening function and the same experimental structure factors and range of temperatures used in the current work. Their agreement was good only at the melting points: all the higher temperature deviated from the experimental values. Silvestrelli *et al.* [27] used *ab initio* molecular dynamics, based on finite-temperature density functional theory, and employed the Kubo-Greenwood formula to calculate the optical conductivity $\sigma(\omega)$ and then extrapolated to the limit $\omega = 0$ to get the static electrical resistivity (similar to work done by Bickham *et al.* [28]) of liquid sodium. Silvestrelli's results were off by an order of magnitude at the melting point but improved at higher temperature (around 850 K). Silvestrelli and coworkers also tried different pseudopotentials in their work and ended up with similar deviations from experimental data. We feel that the Ziman formula provides a more suitable method to calculate the electrical resistivity at and above the melting point and that it yields good agreement with experiment, as shown in Table II.

The thermal conductivity results that we obtained using Eq. (2) were in good agreement with experiment over all temperatures studied. All but two results were within 5%, and the deviations from the Wiedemann–Franz law were fully accounted for by the inelastic part of the electron–phonon scattering and the electron–electron scattering, as shown in Table III. We should note that the model potential can be used to calculate accurately the structure factor of liquid metals using the Monte Carlo method [29–32] or molecular dynamics [33,34]. Thus the calculation can be done completely on a theoretical basis if the experimental structure factor is not available.

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