Electrical Transport in Polyvalent Liquid Bismuth and Antimony Metals

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Accurate assessment of electrical transport for heavy polyvalent metals pause challenge due to complex electronic band structure, where s-wave scattering theory due to Ziman is failed. Improving schemes like t-matrix resistivity and self-consistent approach are proposed. In the present study, we employ self-consistent approach to compute electrical resistivity (ρ) in liquid Bi and Sb at different temperatures (T). Structural input is estimated through charged hard-sphere reference system. Electron-ion interaction is modelled by modified empty-core pseudopotential including electron exchange and correlation effects. Since only two parameters are independent, as the core radius R_C ($= 0.51\ R_a Z^{-1/3}$) is a theoretical input, we have tuned, once and for all, the single parameter to find ρ at melting temperature. The same set of parameters is used to deduce high-T resistivity, thermal conductivity and thermo-electric power. Overall good agreement is observed for transport properties for both metals. The present fitting scheme and so deduced results are discussed in comparison with other findings.

Keywords: Electrical resistivity, Thermoelectric power, Thermal conductivity, Pseudopotential, Liquid metals.

1. INTRODUCTION

The temperature-dependent transport properties of a liquid metal are very important as they are sensitive parameters to structural changes. As direct measurement of transport properties such as electrical resistivity and electrical and thermal conductivity are very complicated, hence theoretical approach is equally important. The electrical transport properties of liquid metals are related to the scattering of electrons which are nearer to Fermi surface. Ziman [1] developed a formalism to describe transport properties of normal metals, which was further extended to transition metals and alloys by Dreirach et al [2]. However, Ziman's formalism cannot be applied to d-state transition metals and polyvalent metals because either the Fermi surface is not perfectly sharp but blurred or due to the closeness of d-band to Fermi surface electrons are tightly bound. Further, the electron mean-free-path in liquid heavy polyvalent metals is larger than interatomic distance, and *weak-interaction* approach due to Ziman is inappropriate. In this connection, self-consistent approximation is frequently used. In the past, self-consistent approach is used by several authors [3, 4] to determine electrical resistivity of liquid metals.

We therefore study electrical transport properties of liquid Bi and Sb metals. Electrical resistivity of liquid antimony is determined by many authors with varying degree of success [5-10], and results for liquid bismuth are scanty. It is known that electrical resistivity depends on electronic band-structure. Bi and Sb are non-simple metals having characteristic that of between *nearly-free-electron* (NFE) system and transition metals. For Sb and Bi electron configuration is $[Kr]4d^{10}5s^25p^3$ and $[Xe]4f^{14}5d^{10}6s^26p^3$, respectively. They are heavy metals having d-band and f-band, re-

spectively; however deep inside a core. Presence of such d-bands and f-bands are important in structural and electronic properties. For instance, structure factor, electrical resistivity, conductivity and thermoelectric power depend on position of d-band and f-band relative to Fermi surface. Bismuth exists in a variety of different structures due to its complex electronic band-structure. Since, Ziman theory cannot be useful to explain transport properties of Bi at high temperature, and Sb for its small mean-free-path; hence self-consistent approach is used to determine transport properties of these liquid metals using pair-wise local pseudopotential including exchange and correlation effect. It is to be noted that model pseudopotential to describe lattice mechanical properties of d- and f-shell metals is proposed by Baria and Jani [11, 12]. It is also used to determine electrical resistivity for simple and non-simple liquid metals. Recently, Patel et al [4] also have calculated electrical transport properties of liquid tetravalent tin metal using local pseudopotential.

In the present paper, we have calculated temperature variation of electrical transport properties including electrical resistivity, thermal conductivity and thermoelectric power for liquid Bi and Sb upto nearly twice their melting temperatures.

2. COMPUTATIONAL METHOD

2.1 Electrical Resistivity

The Ziman [1, 13] approach of investigating electrical resistivity of liquid metals assumes the model of a gas of conduction electrons that interacts and scattered by irregularly placed metal ions. Electrical resistivity for liquid metals within the Ziman theory in terms of local pseudopotential is given by,

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$$\rho_z = \frac{3\pi m^2 \Omega_0}{4e^2 \hbar^3 k_F^6} \int_0^\infty q^3 S(q) W^2(q) \Theta(2k_F - q) dq, \quad (2.1)$$

where m is mass of an electron, e is electronic charge, k_F is Fermi wave vector, Ω_0 is the atomic volume (= reciprocal of number density), $S(q)$ is the static structure factor, $W(q)$ is screened pseudopotential, and unit step function $\Theta(2k_F - q)$ corresponds to Fermi surface, and it is defined as

$$\Theta(2k_F - q) = 0 \text{ for } q > 2k_F;$$
$$\Theta(2k_F - q) = 1 \text{ for } q \le 2k_F.$$

Hence, for limit $q = 0$ to $2k_F$, Eq.(2.1) becomes

$$\rho_z = \frac{3\pi m^2 \Omega_0}{4e^2 \hbar^3 k_F^6} \int_0^{2k} S(q) W^2(q) q^3 dq. \quad (2.2)$$

Eq.(2.2) assumes infinitely long mean-free-path for conduction electrons. Further, the Fermi surface is not perfectly sharp as implied by the Eq.(2.2) but it is blurred in actual. In order to discuss how the resistivity changes with temperature, the density and the average number of electrons per atom Z must be known, which determines the upper limit of resistivity integral. Ferraz and March [14] have modified above equation to include the finiteness of mean-free-path as,

$$\rho_{sc} = \frac{3\pi m^2 \Omega_0}{4e^2 \hbar^3 k_F^6} \int_0^\infty S(q) W^2(q) q^4 \Gamma(q, k_F, l) dq, \quad (2.3)$$

where $\Gamma(q, k_F, l)$ is a function defined by Laakkonen and Nieminen [15], and Khajil and Tomak [16] which takes care of finite mean-free-path. The function $\Gamma(q, k_F, l)$ is given as

$$\Gamma(q, k_F, l) = \frac{2}{\pi q^3} \Big[\tan^{-1}(ql) - A - B \Big], \quad (2.4)$$

where

$$A = \frac{1}{2} \tan^{-1} \left(\frac{2ql}{1 + 4(k_F l)^2 - (ql)^2} \right), \quad (2.5)$$

and

$$B = \frac{\pi}{2} \Theta \left(q - \left(\frac{1}{l^2} + 4k_F^2 \right)^{1/2} \right). \quad (2.6)$$

Mean-free-path (l) can be determined by Drude's formula during each iteration,

$$l = \frac{\hbar k_F}{ne^2 \rho_z}. \quad (2.7)$$

$W(q)$ in Eq.(2.1) is a local pseudopotential due to Hasegawa et al [17], which in $\boldsymbol{q}$-space is given by

$$W(q) = \frac{-4\pi Ze^2}{q^2} \cos(qR_c) X, \quad (2.8)$$

with

$$X = \left[1 + \frac{aq^2}{(q^2 + b^2)} \exp(-bR_c)(1 + \tan(qR_c)) \right].$$

Potential parameters a and b are fitted for the core radius $R_C = 0.51 \cdot R_a Z^{-1/3}$, as explained by Hasegawa et al [17]. Patel et al [18] have also used Hasegawa potential to determine transport properties of liquid Rb. Here, R_a is an atomic radius, Z is valency (we have taken $Z = 5$ for both Bi and Sb), and $S(q)$ is a structure factor. This theoretical input is computed using charged hard sphere (CHS) reference system [19].

2.2 Thermal Conductivity

Thermal conductivity can be given by Weidmann-Franz law [20].

$$\sigma_{th} = \frac{\pi^2 k_B^2 T}{3e^2 \rho_{sc}}. \quad (2.9)$$

Here, ρ_{sc} is resistivity calculated by self-consistent method, Eq.(2.3). Weidmann-Franz law states that the ratio of electronic thermal conductivity over electrical conductivity is constant at high temperatures. At finite-T small $\boldsymbol{q}$- scattering values are possible and electron can be transported without transporting the thermal excitation. At high temperatures phonon contribution to thermal transport remains same and hence the Lorentz number remains constant.

Table 1 – Pseudopotential parameters

Metal	Z	Hasegawa et al [17]		Fitted parameters	
		a	b	a	b
Bi	5	10	2.6	7	2.14
Sb	5	9.5	2.5	5.3	2.07

2.3 Thermoelectric Power

The calculations of the resistivity and thermoelectric power were carried out essentially as described by Evans [21]. Thermoelectric power can be given as

$$Q = -\frac{\pi^2 k_F^2 T}{3E_F} \left(3 - \frac{2S(q)W^2(q)}{\rho} \right), \quad (2.10)$$

where $E_F = \hbar^2 k_F^2/2m^*$ is the Fermi energy, m^* is an effective mass and k_F is the Fermi wavevector. In the past, m^* was calculated from the electron band structure from the ordered crystalline state. However, since we have not done any band structure calculation (pertaining to solid-phase), we take $m^* = m = 1/2$ (in a.u.). Here, m is nominal mass of electron. $S(q)$ and $W(q)$ appearing in above equation corresponds to $q = 2k_F$.

3. RESULTS AND DISCUSSIONS

We have calculated electrical resistivity for liquid bismuth and liquid antimony in terms of self-consistent approach. And thereby we have determined thermal conductivity and thermoelectric power as a function of temperature by taking experimental atomic volume

(Ω_0) at different temperatures [22, 23]. The temperature dependence of resistivity can be explained in connection with the change in the density fluctuation with temperature due to the thermal motion of ions. Next, the calculated values of electrical resistivity and thermal conductivity are compared with other available data.

We have used the modified empty-core potential due to Hasegawa et al [17], and the potential parameters are chosen to yield the good agreement with the experimental electrical resistivity at normal melting temperatures. However, we get good results upto very high temperatures. Calculated values are close to the experimental findings and other results.

Table 1 shows the pseudopotential parameters due to Hasegawa et al [17] and the one which we obtain in present study. It is to be recalled that based on the NFE character of mono- and di-valent alkali and alkaline metals and polyvalent ones, authors in Ref. [17] have classified metals into two categories: simple one and non-simple metals. We choose parameters from the latter categories using the available experimental values of atomic volume (Ω_0) for different temperatures, and thereby core radii were estimated.

Temperature variation of electrical resistivity using the self-consistent approach is plotted in Fig. 1 and Fig. 2 for Bi and Sb, respectively. Present results are compared with experimental and other such theoretical findings. At higher temperatures atoms in liquid metals move with larger amplitude and results in disordered structure and hence the peak of $S(q)$ broadens, whereas the position remains almost unaltered.

This results into reduction in co-ordination number, and hence the *free-volume* available to the charge carriers increases. This explains the increase in resistivity with temperature in Figs. 1 and 2.

It is important to note that the results for electrical resistivity obtained using original set of parameters due to Hasegawa et al [17] differ by 23% and 29% high compared to the other values for Bi and Sb, respectively. It is thus observed from the present results that the self-consistent approach is a better choice for the electrical resistivity and thermoelectric power calculations of non-simple liquid metals using local pseudopotential, when parameters are judicially fitted.
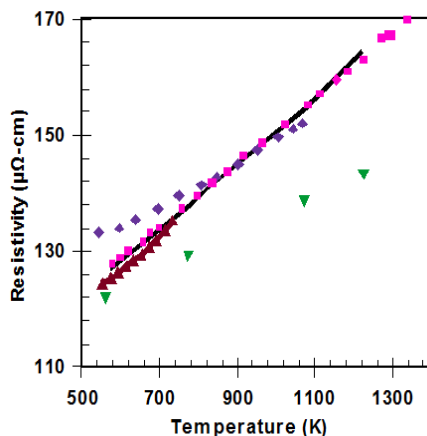

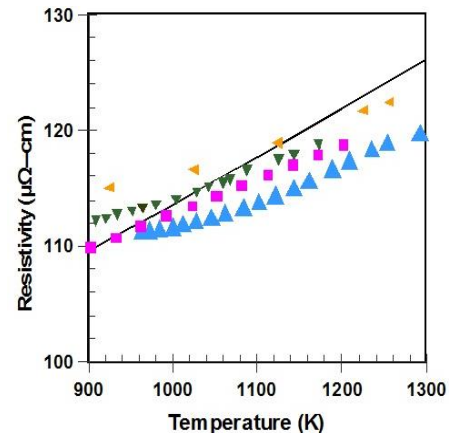**Fig. 2 –** (colour on-line) Temperature variation of electrical resistivity of Sb: Solid line-Present work, ◄ – [5], ▼ – [26], ■ – [7], ▲ – [27]

Fig. 3 and Fig. 4 show temperature variation of thermal conductivity of Bi and Sb, respectively. At high temperatures, *T*-dependence of electrical resistivity and thermal conductivity is largely due to lattice vibrations. As Eq. (2.9) is valid (above Debye temperature) when the scattering of electrons is elastic and relaxation time is independent of energy. Since, we found good agreement
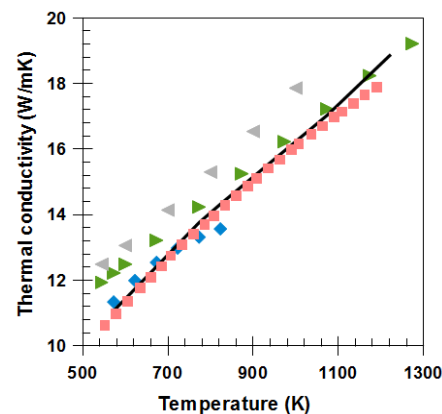

Fig. 3 – (colour on-line) Temperature variation of thermal conductivity of Bi: Solid line-Present work, ◄ – [28], ► – [29], ♦ – [30], ■ – [20]

Fig. 1 – (colour on-line) Temperature variation of electrical resistivity of Bi: Solid line-Present work, ♦ – [9], ▼ – [22], ■ – [24], ▲ – [25]
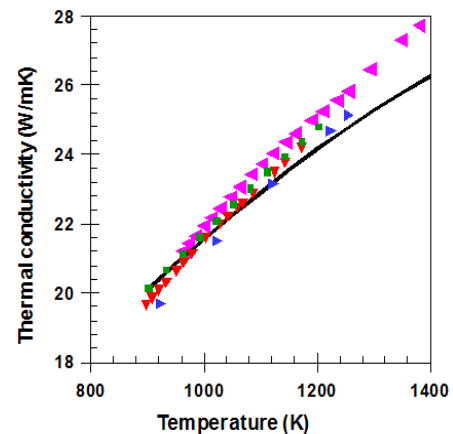
Fig. 4 – (colour -on-line) Temperature variation of thermal conductivity of Sb: Solid line-Present work, ► – [5], ▼ – [26], ■ – [7] and ◄ – [27]. (See text for more details.)
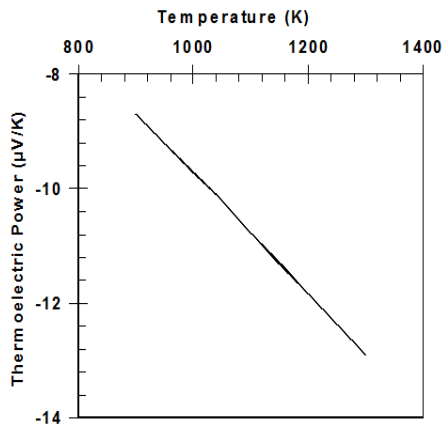
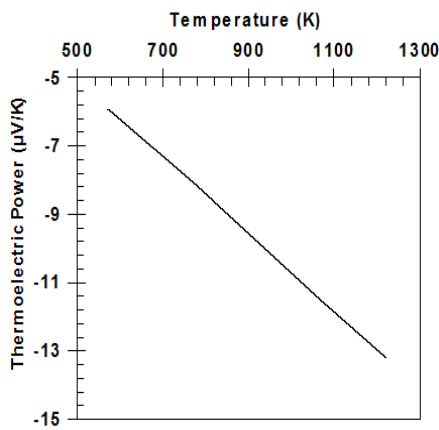**Fig. 5 –** Temperature variation of thermoelectric power for Bi

Fig. 6 – Temperature variation of thermoelectric power for Sb

with experimental results and other findings for both the metals upto very high temperatures; this justifies the use of Weidmann-Franz law. It also suggests that the scattering is predominantly elastic and does not include thermal transport significantly.

We obtain nonlinear increase in thermal conductivity vs temperature curve for Sb as shown in Fig. 4. In lieu of other data for thermal conductivity to us for Sb, we have used Eq. (2.5) to compute the same using respective electrical resistivity data. For instance, in Fig.4; we have also shown thermal conductivity results so calculated from resistivity data of Ref. [5, 7, 26, 27]. We find good agreement with experimental results and other findings for both the metals.

Fig. 5 and Fig. 6 show thermoelectric power for Bi

and Sb as a function of temperature. It is negative over the entire range of temperature and linearly decreasing with a slope dQ/dT − 0.01122 μV/K^2 and − 0.01039 μV/K^2 for Bi and Sb, respectively. Due to unavailability of the experimental data to us, we could not compare the thermoelectric power with other results.

4. CONCLUSION

Calculated electrical resistivity and thermal conductivity results are compared with experimental and other findings. Calculated values of electrical resistivity and thermal conductivity using original parameters of Hasegawa's potential differ by 23% in resistivity for Bi and about 29% that of the Sb. Esposito et al [31] proposed that the Ziman's formulation explains the electrical transport properties properly for simple liquid metals while self-consistent approach results over estimate, if mean-free-paths are smaller than interatomic distances. This is observed in the d-shell metals. In the past, electrical resistivity and hence thermal conductivity were calculated by t-matrix approximation. We have fitted potential parameters to obtain more accurate results. At high temperature our results overestimate the reported data with a difference of about 5%. However, overall agreement is satisfactory. Temperature coefficient of resistivity $d\rho/dT$ for Sb is found to be 0.041 $\mu\Omega cm$/K, which is as high as 27% compared to results in [8]. But for Bi, we obtain good correlation with other all findings, and are better in some cases. Calculated values of electrical resistivity for both Sb and Bi are in good agreement with experimental findings and other results. Due to small electronic mean-free-path and good results for electrical resistivity and thermal conductivity for liquid polyvalent antimony and also for bismuth suggest that they should be treated as d-band-like (non-simple) metals while evaluating their electrical transport properties. This justifies the use of self-consistent approach (which includes the blurring effect of Fermi surface at high-T) in conjunction with an effective single-parameter local pseudopotential.

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