

ANALYSIS OF THERMOELECTRIC POWER OF Li, Na & K LIQUID ALKALI METALS

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ABSTRACT

Thermoelectric power of Li, Na & K liquid alkali metals have been studied using pseudo potential approach. The present study concludes that the recent value of the thermoelectric power departs only by 3% from its experimental value and does not require any arbitrary reduction of V_{opw} as $(3 = 1)$. This method gives uniformly good agreement for these alkali metals.

Key words:- Parameterized model potentials, Core wave function, Phonon wave vector, Fermi wave vector, Phonon frequency, Thermoelectric power.

INTRODUCTION

In the analysis of physical properties of metals Parameterized model potentials have been widely used by Heine and Weaire [Solid State Physics, Vol.-24, p. 3 (1970)]. For the calculations the parameters have generality been adjusted to some gross property of metals. Harrison's first principle method ["Pseudopotential in the theory of metals" (W. A. Benjamin, Inc. New York, 1966)] provides the crystal potential involving the energy value and eigen function of core electrons. In this scheme core electron eigen functions are generally assumed to be identical in the metal and in the free ion [Phys. Rev., 135, A-1363, (1965)].

This approach has been applied by Cutler *et al* [J. Phys. F 5, 1801 (1975)] to the study of phonon frequencies of alkali metals. Hafner [J. Physics., F 5, L- 150,] has studied the phonon dispersion relation for lithium and sodium with Vashista and Singwi's [Phys. Rev. B 6, 875, (1972)] exchange and correlation. They have modified the V_{opw}

appearing in Harrison's formalism by multiplying it by a factor β equal to 5/8. Although the approach has presented a good picture of phonon dispersion relations, it has not been applied to the study of thermoelectric power of liquid alkali metals. This property sensibly depends on form factor near $q = 2k_F$ and their study may be important in assessing the performance of the approach. We have therefore calculated the form factors of lithium and sodium using Hafner's [J. Physics., F 5, L-150,] energy values and his a and J with Vashishta and Singwi's [Phys. Rev. B 6, 875, (1972)] exchange and correlation and used them to study the thermoelectric power of (Li and Na) by Zim's formula [Phill. Mag. 6, 1013, (1961); Adv. Phys., 16, 551, (1967)]. Further the calculations have also been repeated with $\beta = 1$ and Slater's ["Quantum theory of molecules and atoms" (McGraw-Hill Pub. Co. Inc. New York, 1972) (p. 27)] values of $a = 0.78147$ for lithium and 0.73115 for sodium. The result obtained with Slater's values ["Quantum theory of molecules and atoms" (Mc

Graw-Hill Pub. Co. Inc. New York, 1972) (p. 27)] agree well with the experimental values of thermoelectric power and do not require any arbitrary reduction of V_{opw} .

2 Computation of form-factor:

The screened form factor is expressed-as

$$\langle k+q | w | k \rangle = \frac{V_q^{ab} + V_q^c + V_q^d + V_q^f}{\epsilon^*(q)}$$

$$+ \langle k+q | w^R | k \rangle = -G V_q^{-1} / \epsilon^*(q) \quad (1)$$

where V_q^{ab} are the valence charge and core

potentials, V_q^c is the conduction-band-core

exchange potential. V_q^d , the conduction electron potential. Expression for these have been taken from Harrison ["Pseudopotential in the theory of metals" (W. A. Benjamin,

Inc. New York, 1966).] V_q^d arises from the screening of the repulsive potential $\langle k+q | w^R | k \rangle$ and is defined by Harrison ["Pseudopotential in the theory of metals" (W. A. Benjamin, Inc. New York, 1966).].

$$\epsilon^*(q) = 1 + (1-G(q))(\epsilon(q)-1) \quad (2)$$

$G(q)$ takes into account the effect of exchange and correlation among conduction electrons for which Vashishta and Singwi's [Phys. Rev. B 6, 875, (1972)] from $G(q) = A(1 - e^{-Bq})$ has been used.

The constants A and B for the metals are $A = 1.00714$ and $B = 6.2986$ (for Lithium) and $A = 1.00778$ and $B = 0.2855$ (for sodium), $\epsilon(q)$ is the Hartree - dielectric function given by

$$\epsilon(q) = 1 + \frac{2}{\eta^2 k_F} \left\{ \frac{4 - \eta^2}{4\eta} |n| \frac{\eta + 2}{\eta^{-2}} + 1 \right\} \quad (3)$$

where $\eta = q/k_F$, q and k_F are the phonon wave vector and Fermi wave vector respectively. Other terms appearing in equation (1) are the same as those of Harrison ["Pseudopotential in the theory of metals" (W. A. Benjamin, Inc. New York, 1966).].

The repulsive potential $\langle k+q | w^R | k \rangle$ involves f_{ni} given by

$$f_{ni} = (-3.6 Z/r_0) + V_O^b + V_O^c - V_{qpw} + |e_{ni}| \quad (4)$$

A modification of equation (1) for Harrison's form factor has been done in respect of V_{opw}

appearing in equation (4) and V_q^a appearing in equation (1)

V_{opw} has been replaced by

$$V_{opw}^* = \beta V_{opw}$$

where

$$V_{opw} = -\frac{\Omega}{\pi^2} \sum_{nl} (2l+1) \left[\frac{P_{nl}^2(r)}{r} \right] \int_0^{k_F} k^2 \langle k | n | k \rangle^2 dk$$

where $P_{nl}(r)$ is the radial part of the core wave function, V_q^c has been replaced by Slater's

X α - exchange. In the present calculation we have considered $\alpha = 1$ (Slater [Phys. Rev., 81, 385, (1951)] with $\beta = 5/8$ (Hafner [J. Physics., F 5, L-150]), and $a = 0.78147$ (Slater ["Quantum theory of molecules and atoms" (Mc-Graw-Hill Pub. Co. Inc. New York, 1972) (p. 27)]) with $\beta = 1$ for Lithium.

We have also used $\alpha = 2/3$ (Kohn and Sham [Phys. Rev., 140, A-1133 (1965)]) with $\beta = 5/8$ (Hafner [J. Physics., F 5, L-150, J-], and $a = 73115$ (Slater ["Quantum theory of molecules and atoms" (McGraw-Hill Pub. Co. Inc. New York, 1972) (p. 27)]) with $\beta = 1$ for Sodium to get a more comprehensive view of the performance of the approach.

The values of e_{ni} are from Hafner [J. Physics., F 5, L-150]. In their evaluation the atomic wave functions tabulated by Herman and Skillman ["Atomic structure calculation"

(Prentice-Hall, New York, 1963)] have been used.

3. Computation of thermoelectric power

Thermoelectric power may be obtained from the expression of the electrical resistivity by differentiating it with respect to the energy at the Fermi level. As the isothermal compressibility of alkali metals by the use of the nearly free electron approximation, Ziman [Phil. Mag. 6, 1013, (1961); Adv. Phys., 16, 551, (1967)] has given an expression for the computation of the electrical resistivity, which is given as

$$R = \frac{3\pi}{he^2 V_F^2 N(E_F)} \int_0^1 4 |< k+q | w | k >|^2 a(q) \left(\frac{q}{2k_F}\right)^2 d\left(\frac{q}{2k_F}\right)$$

where V_F the Fermi velocity and $a(q)$ the liquid structure factor.

The liquid structure factor needed in the calculation is taken from the work of Gingrich and Heaton [J. Chem. Phys. 34, 873, (1961)] for Lithium and Greenfield *et al.* [Phys. Rev., A-4, 1607 (1971)] for sodium.

Thus the absolute value of thermoelectric power, Q , at the absolute temperature, T , can be written as

$$Q = (\pi^2 k_B^2 T / 3 |e| E_F) X \quad (5)$$

where e is the electronic charge, k_B in the Boltzmann constant, E_F is the free electron Fermi energy and X is a dimensionless parameter and is known as the thermopower coefficient defined by

$$X = -E_F |\partial \ln R(E) / \partial E|_{E=E_F} \quad (6)$$

where $R(E)$ is the electrical resistivity, Bradley *et al.* [Phil. Mag. 7, 865 (1962)] have expressed X as

$$X = (3 - 2p - r/2) \quad (7)$$

where,

$$p = \frac{IW(k_F, 2k_F) I^2 a(2k_F)}{a(q) |N< k+q | w | k >|^2} \quad (8)$$

and

$$r = \frac{k_F < a(q) \partial / \partial k | < k+q | w | k >|^2 >}{< a(q) | < k+q | w | k >|^2 >} \quad (9)$$

Here $W(k_F, 2k_F)$ stands for the value of the form factor at $k = k_F$ and $q = 2k_F$, $< >$ stands for an average of the form

$$< a(q) | N < k+q | w | k >|^2 >$$

$$\int_0^1 4 |N < k+q | w | k >|^2 a(q) \left(\frac{q}{2k_F}\right)^3 d\left(\frac{q}{2k_F}\right)$$

(10)

where k refers to the wave vector of the incident electrons and is taken to be k_F in the evaluation

$$\partial N / \partial k < k+q | w | k > = k_F \sum_{nl} 2(2l+1)$$

$$P_1(\cos\theta) | k = k_F < k_F | n | o >^2$$

$$+ 2k_F \sum_{nl} (2l+1) \{ < k_F | n | o >^2 + (k_F^2 + f_{nl}) < k_F$$

$$| n | o > \partial < k_F | n | o > / \partial k$$

$$X = \frac{\sum (2l+1) < k_F | n | o >^2 + P_1(\cos\theta)}{1 - \sum_{nl} (2l+1) < k_F | n | o >^2}$$

$$\sum_{nl} (k_F^2 + f_{nl}) (2l+1) < k_F | n | o >^2$$

$$\frac{\sum (2l+1) < k_F | n | o >^2 + P_1(\cos\theta) |_{k=k_F}}{(1 - \sum_{nl} (2l+1) < k_F | n | o >^2)^2}$$

$$X = \sum 2(2l+1) < k_F | n | o > \partial < k | n | o > / \partial k |_{k=k_F}$$

where k refers to the wave vector of the

incident electron and is taken to be k_F in the evaluation.

RESULTS AND DISCUSSION

The thermoelectric power of alkali metals (Li, Na, and K) at melting point has been calculated through the equation (5)

Table 1 gives the constants for Li and Na, computed form factors of Li and Na with different values of α and β are given in Table 1. Table - 3 and 4 present the results of the thermoelectric power of Li and Na respectively calculated on the basis of equation -(5). The experimental values are incorporated for comparison.

Table-1. Constants and other quantities (In atomic units) and energy (In Ryd) For

Li and Na		
Quantity	Lithium	Sodium
Ω	153.3335	273.0258
K_F	0.5781	0.4741
Z^*	7.07207	1.07254
V_0^b	-0.02323	-0.02034
V_0^c	-0.17448	-0.21125
V_{OPW}	-0.34085	-0.27038

It may be noted that Hafner used the value of $\alpha = 1$ [Phys. Rev., 81, 3185, (1951)] which necessitated to reduce the V_{OPW} arbitrarily by a factor $\beta = 5/8$ in order to set excellent agreement with the experimental phonon frequency. But the recent values of $\alpha = 0.78147$ ["Quantum theory of molecules and atoms" (McGraw-Hill Pub. Co. Inc. New York, 1972) (P-27)] on the basis of the generalized statistical exchange approximation with $\beta = 1$ gives consistently good results for the thermoelectric power. This does not require any arbitrary reduction of V_{OPW} as was done by Hafner.

Table-4. also demonstrates the same effect for Na. Hafner has taken $\alpha = 2/3$ of Kohn and Sham (Phys. Rev., 140, A-1133 (1965)) and here also he has to take $\beta = 5/8$ in order to get better agreement in the phonon frequency. The calculated thermoelectric power comes out to be -7.14 $\Omega V/K$ whereas the reported experimental values is -9.9 (Cusack, Rep. Progr. Physics, 26, 361(1963)) and -8.9 $\Omega V/K$ (Bradley, Phil. Mag., 7, 1337 (1962)). If one takes the recent value of $\alpha = 0.73115$ (9) with $\beta = 1$, the thermoelectric power comes out to be -10.18 $\Omega V/K$. In this case, however the thermoelectric power departs only by 3% from its experimental value and does not require any arbitrary reduction of V_{OPW} as $\beta = 1$.

Table-2. Form - factor (In Ryd) for Li and Na

q/kF	Lithium		Sodium		$\alpha=1$ $\beta = 5/8$
	$\alpha = 0.78147$ $\beta = 1$	$\alpha = 2/3$ $\beta = 5/8$	$\alpha = 0.78147$ $\beta = 1$	$\alpha = 0.78147$ $\beta = 1$	
0.0	-	-	-	-	-
0.2	-0.20142	-0.18877	-0.13772	-0.13772	-0.14652
0.4	-0.17402	-0.15902	-0.12835	-0.12835	-0.13509
0.6	-0.16107	-0.14238	-0.11411	-0.11411	-0.12269
0.8	-0.14433	-0.12139	-0.10246	-0.10246	-0.11082
1.0	-0.12749	-0.10048	-0.08573	-0.08573	-0.09002
1.2	-0.10838	-0.07816	-0.07083	-0.07083	-0.07855
1.4	-0.08437	-0.05221	-0.05321	-0.05321	-0.06052
1.6	-0.04385	-0.01108	-0.03141	-0.03141	-0.03824
1.8	-0.00744	+ 0.02487	-0.01235	-0.01235	-0.01864
2.0	+ 0.03114	+ 0.06235	+ 0.00930	+ 0.00930	+ 0.00362

Table-3. Thermo electric power of $Q(\mu\text{V/K})$ of Lithium

Source	Energy value $\epsilon_n(\text{in Ryd})$	α	β	Q_{cal}	Q_{exp}
Hafner	$\epsilon_{10} = -5.0383$	1	5/8	-0.36	+21.5
(5)	-	0.78147	1	+15.57	-

Table-4. Thermo electric power of $Q(\mu\text{V/K})$ of Sodium

Source	Energy value $\epsilon_n(\text{in Ryd})$	α	β	Q_{cal}	Q_{exp}
Hafner	$\epsilon_{10} = -78.777$	2/3	5/8	-7.14	-9.9(18)
	$\epsilon_{20} = -5.2933$				
	$\epsilon_{21} = -3.2353$	0.73115	1	-10.18	-8.9(19)

The present study concludes that the recent value of Slater's exchange does not require any arbitrary reduction of V_{opw} by a factor ($\beta = 5/8$) as was done by Hafner and Cutler *et al.* at least for the calculation of thermoelectric power.

It has been observed that the thermoelectric powers of Potassium is in poor agreement.

It has been observed from Table 3 that in the case of Lithium for the values of $\alpha = 1$ and $\beta = 5/8$ as used by Hafner the thermoelectric power calculation yields a negative value whereas the experimental value is of positive sign. This makes the situation ambiguous and one cannot accept the combination. Further with the recent value of α equal to 0.78147 (9) and $\beta = 1$, we find that the situation improves considerably. The calculated value of the thermoelectric power comes out to be 15.57 $\mu\text{V/K}$ in comparison with the experimental value of 21.5 $\mu\text{V/K}$ (Cusack, Rep. Progr. Physics, 26, 361(1963)).

The cause behind this low value of thermoelectric power in magnitude in the

case of K is the higher value of form-factor at $q = 2K_F$. This increases the value of P in Bradley *et al.*'s formula (equation-8) and hence in turn reduces the value of thermoelectric power coefficient (X).

Table-5. Experimental static structure $a(q)$ of Alkali metal near melting point

q/k_F	Li	Na	K
Temp. °C	180	100	65
→			
0.0	0.0735	0.0240	0.0247
0.2	0.080	0.02481	0.0247
0.4	0.090	0.02699	0.02942
0.6	0.1033	0.03030	0.03330
0.8	0.120	0.03517	0.0388
1.0	0.140	0.04387	0.0471
1.2	0.1848	0.06002	0.0608
1.4	0.2450	0.08733	0.0883
1.6	0.3540	0.14331	0.15107
1.8	0.5620	0.29763	0.3310
2.0	1.2150	0.87895	1.0291

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