Study on the Requirement of Inclusion of Atomic Number in Optimized Model Potential (OMP) for Thermoelectric Power in Alkali Metals

Dhirendra Kumar, Prakash Nayak

***Abstract*— A close look on experimental values of thermoelectric power and electrical resistivities of alkali metals shows dependence of these properties on the atomic numbers of metals in some form. This may suggest that, contrary to the present belief, the charge on the bare unscreened nucleus has important bearing on the properties of metals. The marked disagreement in the calculated values based on improved Optimized Model Potential (OMP) and experimental values of thermoelectric power in most of the alkali metals, except in case of sodium and potassium, also points in the same direction and suggest that model potentials should include in some form the atomic number in their structure.**

***Index Terms*— Thermoelectric power, electrical resistivity, Optimized Model Potential (OMP), alkali metals and atomic number.**

I. INTRODUCTION

The interaction of the conduction electrons with the lattice vibration is at the centre of the whole theory of transport properties. It determines electrical and thermal conductivity at ordinary temperature and is the source of thermoelectric effects at high and low temperatures. The alkali metals with one conduction electron per atom and which are known to be approximately free electron – like, appears to be an ideal candidate for the examination of transport properties. It was recognised that phonon drag was responsible for most of the anomalies found in thermopower of pure alkali metals at low temperatures; its sign presented a problem which was only in the early stages of being resolved. We have tried to show that the charge on bare unscreened nucleus has important bearing on the properties of metals and show the optimized model potential should include in some form the atomic numbers in their structures. Following closely the work of Shaw (Shaw, R. W.,!968) Appapillai and Williams have described the construction of improved optimized model potential (OMP) in solids (Appapillai and Williams, A. R., 1973). They corrected Shaw OMP in respect of

(a) The energy dependence and nonlocally of diagonal matrix element of the potential by using effective masses as discussed by (Shaw, 1969).
(b) Depletion hole charge and
(c) Exchange and co- relation among the conduction electron.

II. COMPARISON OF CALCULATED AND EXPERIMENTAL THERMOELECTRIC POWER OF ALKALI METALS

Thermoelectric power and phonon frequencies of alkali metals have not been explored by the refined OMP suggested by Appapillai and Williams.

The thermoelectric power (S) at temperature is obtained from

$$S = -\frac{\pi^2 K_B^2}{3|e|\, E_F}\, X \qquad \text{.............} \quad (1)$$

Where K_B is Boltzmann constant, E_F is the free electron Fermi energy and X is given by Bradley et al (1962) as

$$X = 3 - 2P^{-\frac{1}{2}} \qquad \text{...............} \ (2)$$

Where

$$p = \frac{|W(K_F \cdot 2K_F)|^2\, a(2K_F)}{\langle a(q)|W(K,q)|^2\rangle} \qquad \text{...............} \ (3)$$

and

$$r = \frac{K_F \langle a(q)\frac{\partial}{\partial K}|w(K,q)|^2\rangle}{\langle a(q)|w(K,q)|^2\rangle} \qquad \text{...............} \ (4)$$

Here < > stands for an average of the form

$$\langle a(q)|W(K,q)|^2\rangle = \int_0^1 d\left(\frac{q}{2K_F}\right) 4\,|W(K,q)|\left(\frac{q}{2K_F}\right)^3 a(q) \qquad \text{...............} \ (5)$$

Where K refers to the wave vector of the incident electron and is taken to be K_F; W (k, q) is the screened form vector: a (q) is the structure vector, and is taken from measurement of Gingrich and Heaton (1971) for Li, Rb and Cs and from Greenfield et. al (1971) for Na and K. The form factor W (k, q) may be obtained in the manner described by Appapillai and Williams (1973).

The experiments and calculated values of thermoelectric power along with the data used in the calculation are presented in table 1.

Element	**K_F / au**	**Melting Point K**	**Thermoelectric power μvk**	
			Present calculation	**Experimental**
Li	0.578	453	+36.3	+21.5
Na	0.474	373	-7.87	-9.9
K	0.383	338	-14.40	-15.5
Rb	0.357	312	-15.70	-7.7
Cs	0.332	303	-15.86	+6.4

Table 1: Thermoelectric power and related data

The table 1 shows that although the calculated thermoelectric power for sodium and potassium are closed to the experimental values, the result for the other alkali metals are marked disagreement, the two differing by about 75% in case of lithium and 100 % in case of rubidium. Further the calculated value of thermoelectric power of cesium is the negative sign instead of being positive as given by experimental measurement.

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III. COMPARISON OF CALCULATED AND EXPERIMENTAL PHONON FREQUENCIES OF ALKALI METALS

Using Ewald's method for determining Coulomb's interaction between ions and taking energy wave number characteristics from Appapillai and Williams (1973) phonon frequencies of alkali metals have been calculated as compared with experimental values.

In the harmonic approximation, the phonon frequency of a cubic solid are calculated from a secular equation of the type

$$\left| D_{\alpha\beta}(q) - MW^2\delta_{\alpha\beta} \right| = 0 \qquad \text{.......... (6)}$$

Where $D_{\alpha\beta}(q)$ are the element of the dynamical matrix, q is the phonon wave vector and M is the mass of the ion.

The element $D_{\alpha\beta}(q)$ of the dynamical matrix are expressed as the sum of three terms as

$$D_{\alpha\beta}(q) = D^c_{\alpha\beta}(q) + D^\gamma_{\alpha\beta}(q) + D^b_{\alpha\beta}(q) \qquad \text{.............. (7)}$$

Where the superscripts c, γ, b and Dαβ (q) are the Coulombic, repulsive and band structure parts respectively. In the case of cubic crystal the secular equation factorizes in three principal symmetry directions and one obtains

$$W^2(q) = W_c^2(q) + W_\gamma^2(q) + W_b^2(q) \qquad \text{…........... (8)}$$

$W_c^2(q)$ which arises from the direct Coulomb's interaction between ions, has been determined by Ewald's method. (Ewald, P. P., 1921). While the second term $W_\gamma^2(q)$ is responsible for exchange repulsion between ions has been neglected here (Vosko, S. H. 1964). The band structure part which takes into account of electron – ion interaction can be expressed as (Vosko, S. H. 1965)

$$W_b^2(q) = W_p^2\left[\sum_h A(q+h) - \sum_n A(h)\right] \qquad \text{…........... (9)}$$

Where $A(q) = (\epsilon \cdot q)^2 F\frac{(q)}{q^2}$, ϵ is the polarisation vector, h represent the reciprocal lattice vector and W_P is the plasma frequency in C. G. S. Units. F (q) is the energy wave number characteristics taken from Appapillai and Williams (1973) data.

The calculated values of phonon frequencies for potassium and rubidium are plotted in Figure 1 along with the respective experimental values of potassium. (Cowley, R. A. et. al, 1966) and rubidium (Copley, J. R. D. 1973). Phonon spectra of cesium are shown in figure 2. As no experimental values are available, the results are compared with the values obtained by (Shrivastava, P. L. et. al 1976) using the relation

$$\upsilon_n(q) = N^{-m} C(q, \epsilon) \qquad \text{........... (10)}$$

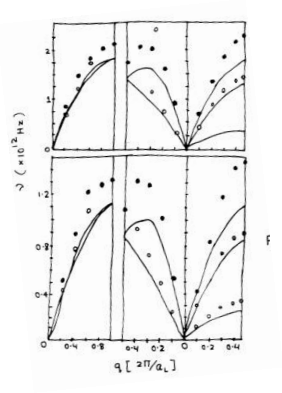

Figure 1(a): Phonon dispersion relation for potassium and 1(b): Phonon dispersion for rubidium

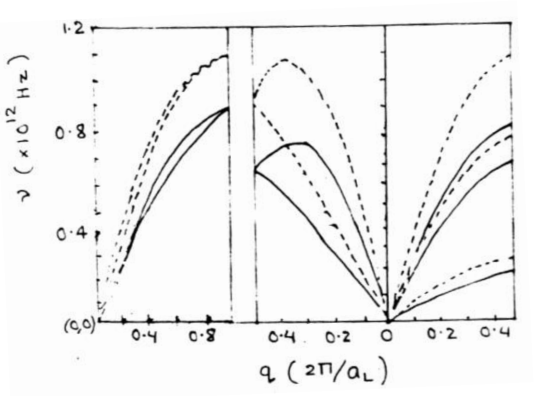

Figure 2: Phonon dispersion relation for Cesium

Where $\upsilon_n(q)$ is the phonon frequency corresponding to atomic number n.; m and C (q, ϵ) depends on a phonon wave vector q and polarization ϵ.

IV. RESULT AND DISCUSSION

From table 1 it is evident that the calculated results of thermoelectric power show poor agreement with the experimental values except in case of sodium and potassium. The same pattern of disagreement is also shown by the electrical resistivities.

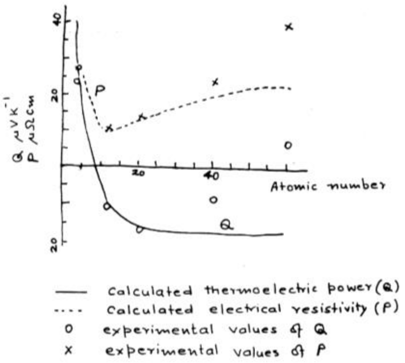

Figure 3: Plot of thermoelectric power and electrical resistivity of alkali metals against their atomic numbers.

This has been diagrammatically presented in figure 3 in which the calculated and experimental values of thermoelectric power and electrical resistivities (from table of the paper by Williams and Appapillai, 1973 have been plotted against the atomic numbers of the metals. It is interesting to note that figure 3 indicates the dependence of these parameters on the atomic number of metals in some form. Contrary to the present belief, this suggests that the charge on the bare unscreened nucleus has important bearing on the properties of metals.

The calculated frequencies shown in figure 1 differ significantly with the experimental values deviating about 25% at the zone boundary. Further, we notice that the crossover of the longitudinal branch by the transverse one in 100 directions is exhibited in all alkali metals. Such a feature is also displayed by the experimental results prominently in the case of lithium and less significantly in the case of sodium. It may be noted that Coulthard (1970) has obtained better results of phonon frequencies for sodium, potassium and aluminium using refined Shaw model with Shaw and Pynn (1969) exchange. It is perhaps due to form of exchange as pointed out by William's and Appapillai. Its appears that gain if any, by incorporating effective mass correction to the Shaw model which is not likely to affect the phonon frequencies sensibly (Bertoni, et. al, 1974) has been offset by the form of exchange used by Appapillai and Williams.

Elements	Li	Na	K	Rb	Cs
X(Experimental)	-8.8	2.9	3.5	1.7	-1.3
X(sandstorm, 1965)	-7.7	2.9	3.1	1.4	1.2
X(Young, Mayer and Kilbey, 1967)	-5.0	0.6	2.8	0.1	-7.8

Table 2: Experimental and theoretical values for the thermoelectric parameters X of liquid alkali metals

V. CONCLUSION

Experimental and theoretical values for the thermoelectric parameters X of liquid alkali metals has been presented in in table 2. It should be noted that negative values of X indicate positive thermopower. Two principle anamolies occur in these metals for which explanation are required. These are

1. The existence of negative values of X in Cesium and Lithium and

2. The values of X in potassium which is greater than the expected maximum values of 3.

As far as negative values of X are concerned observation of basics expression 2, 3 and 4 shows, disregarding last term for the present, that negative values of X are quite possible should be sufficient large.

$$|W(2K_F)|^2 \, a(2K_F)$$

The monovalent metals are in a particular favourable position to have high values of the structure factor a(2K$_F$) which could easily rise to as high as -3 at the first peak and although W(k, q) changes through zero near 2K$_F$, its magnitude at 2K$_F$ could be sufficient to make 2p>3 (Bernard, 1969). One might except quite large variation in the sign and magnitude of X where pseudo – potential is large. The large variation in X are clearly evident from the data given in table 3 with X decreasing as we move away from sodium and potassium towards the heavier alkalis rubudium and cesium and towards the lighter alkali metal lithium.

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Dhirendra Kumar:

I did my Post Graduation in Physics with First Class in 1987. Since then I am involved in research and teaching work. I obtained Ph. D degree from L. N. Mithila University in 2001. Throughout my professional career, I have been engaged and associated with several research works resulted in publication of more than 15 research papers in various Journals of International repute. Over the years, I have attended and presented papers in many seminars and workshops. I am life member of ISCA (Indian Science Congress Association) and LASSI (Laser and Spectroscopy Society of India, BHU). I worked as Project Fellow of the Major Research Project UGC under Principal Investigator Dr. Prakash Nayak .Working as Project Fellow at R K College, Madhubani, I engaged PG classes in Physics to the satisfaction of all. Recently both of us have jointly undertaken to write books also and one is in the stage of printing. My research and UG teaching experience is of nearly 25years. My field of research is Microstrip patch antenna and photonic band gap structures. In addition, I am counsellor with IGNOU.

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I did my PG in Physics from Bihar University in 1977 obtaining second position in the University among First class. Subsequently I joined as lecturer in the Department of Physics at R. K. College, Madhubani (a constituent unit under L. N. Mithila University) in 1980 under VC appointment. I started my research work and under UGC Faculty improvement programme obtained Ph. D degree in 1990. I guided research work successfully leading to award of Ph. D degree to my scholar. I have remained actively engaged in research work leading to publication of more than 15 research papers in various journals. I was awarded Major Research Project by UGC and worked as Principal Investigator. I have attended so many seminars and presented papers in them. I have also attended workshop in Experimental Physics organized by Araybhatt University. I am life member of ISCA (Indian Science Congress Association) and LASSI (Laser and Spectroscopy Society of India, BHU) . Recently, I have also undertaken to write book and is in the process of publication. I was promoted to the rank of associate professor in 1990. I have UG and PG teaching experience of more than 30years.

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