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Role of core energy eigenvalues in the computation of the electronic transport properties of liquid alkaline earth metals Mg & Ca: HFP Technique

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ABSTRACT

In the present paper we have studied the electrical resistivity (R) and the Knight shift (K%) of liquid alkaline earth metals Mg and Ca using two sets of self consistently computed eigenvalues viz. those of Herman-Skillman (H)[1] and Clementi (C)[2] alongwith the Xα-exchange parameter α_{vt}, satisfying Virial theorem Schwartz[3] orthogonalisation hole parameter $\beta=1$ Harrison[4] and Vashishta-Singwi[5] form of exchange correlation. Reasonable agreement has been obtained with experimental data. The impact of the choice of two sets of eigenvalues on the form factor and the computed properties has been studied.

KEYWORDS

Liquid metal;
Electrical resistivity;
Knight shift;
Pseudopotential;
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INTRODUCTION

Liquid alkaline earth metals have not been extensively studied through Harrison's First Principle (HFP) pseudopotential technique because of s-d hybridization. Moriarty[6,7] has extended the HFP theory including hybridization effect which has improved his resistivity results in some cases. However, in some cases the hybridization effect has not been very successful.

In case Mg the electronic configuration does not contradict the free electron like behavior which has been supported by Faber[8] through mean free path and effective mass considerations. It has been observed that Be and Mg although being in group IIA of the periodic table resemble the elements of group IIB i.e. Zn, Cd and Hg. The similarity with Ca and Sr are not so pronounced in Be and Mg. In comparison to alkali metals the alkaline earth metals have been supposed to be more tedious for treatment due to their non-simple metal like character. Through the present investigation we have shown that if proper choice of core energy eigenvalues is made, the electronic transport properties of Mg and Ca may be predicted reasonabley accurately.

The HFP pseudopotential technique is based on sound theoretical background, no arbitrary model is proposed and no adjustable parameters are introduced to get good agreement of the computed properties. The basic input parameter are the core energy eigenvalues ϵ_{nl}, the radial wave functions $P_{nl}(r)$ are evolved through self consistent field approximation. Two such sets are available viz. those of Herman-Skillman[1] and Clementi[2] represented by H and C eigenvalues. It has

TABLE 1a : Table of constants (in a.u.)

Metal	K_F	Ω_0	α_{vt}	β	(V-S) constants		Z
					A	B	
Mg	0.6992	173.2	0.7285	1	1.1318	0.2975	2
Ca	0.5649	328.5	0.7194	1	1.1115	0.2827	2

where K_F – Fermi wave vector, Ω_0 – Atomic volume, α_{vt} - Xα-exchange parameter satisfying Virial theorem, β – opw multiplier, Z – Valence and A,B- (V-S) constants

TABLE 1b : Table of eigenvalues (Ryd) in respect of magnitude

Metal	Author	$\in_{10}$	$\in_{20}$	$\in_{21}$	$\in_{30}$	$\in_{31}$
Mg	H	94.95	6.55	4.14	-	-
	C	98.06	7.53	4.56	-	-
	Exp	96.0	4.63	3.69	-	-
Ca	H	293.52	31.63	26.18	3.87	2.48
	C	298.73	33.64	27.26	4.49	2.68
	Exp	297.40	31.90	25.50	3.10	1.90

TABLE 2 : computed electrical resistivities R (μΩcm)

Metal	$\in_{nl}$	Computed resistivities R(μΩcm)	R_{exp}(μΩcm)
Mg	C	25.9	27.4
	H	52.17	
Ca	C	140.10	33.0
	H	39.9	

where H-with Herman-Skillman's eigenvalues, C-with Clementi's eigenvalues

TABLE 3 : Computed knight shift (K%)

Metal	K_0	$\in_{nl}$	K%	(K%)expt.
Mg	0.13	C	0.15	0.11
Ca	0.31	H	0.55	-

been observed that these sets of eigenvalues are not identical. They differ from each other and also from the experimental values [vide TABLE 1b]. Therefore, it is quite interesting to examine how far these discrepancies of eigenvalues affect the non-local screened form factors w(k,q) and consequently the computed properties viz, the electrical resistivity (R) and Knight shift (K%).

Formalism

The non-local screened form factor obtained through the HFP pseudopotential technique is given by,

$$w(k,q) = v^*_{ab} + v^*_c + v^*_d + v^*_f + w^R \qquad (1)$$

where the quantities on the R.H.S. represents the effective, screened values of the valence charge and core

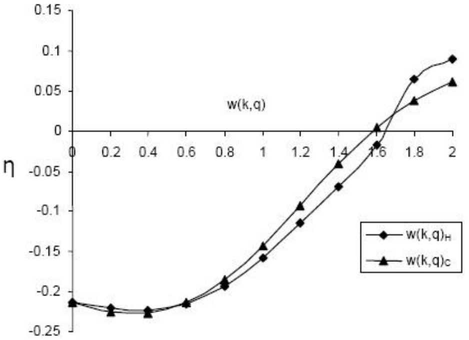

Figure 1 : Nature of the computed form factors w(k,q) of Mg using different eigenvalues alongwith. $\alpha = \alpha_{vt}$ and $\beta = 1$, (V-S) exchange-correlation

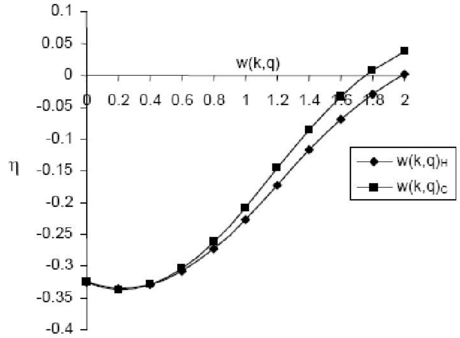

Figure 2: Nature of the computed form factor w(k,q) of Ca using different eigenvalues alongwith. $\alpha = \alpha_{vt}$ and $\beta = 1$, (V-S) exchange-correlation

electron potential, the conduction band-core exchange potential, the conduction electron potential and the screening potential respectively. w^R is the repulsive part of the pseudopotential (vide Harrison[4]).

In the present computation we have used Xα-exchange parameter $\alpha = \alpha_{vt}$ which satisfies the Virial theorem and has been supplied by Schwartz[3]. The orthogonalisation hole parameter $\beta = 1$ has been taken as originally suggested by Harrison[4]. This parameter occurs in the OPW potential V_{OPW}. The exchange correlation function G(q) of Vashishta-Singwi[5] has been used which has been acknowledged to be superior to various other forms as it satisfies the compressibility some rule and gives a better picture of inter ionic pair potential. The experimental structure factor a(q) of Woemer et al.[9] and Waseda et al.[10] has been used for Mg and Ca respectively.

Electrical resistivity

The electrical resistivity (R) has been computed through the well known Ziman's formula[11] given by,

$$R = \frac{3\pi Z\Omega_0}{\hbar e^2 v_F^2}\int_0^1 |w(k,q)|^2 a(q) 4(q/2k_F)^3 d(q/2k_F) \qquad (2)$$

where Ω_o, Z, v_F, k_F, w(k,q) and a(q) are the atomic volume, valence, Fermi energy, Fermi wave vector, form factor and structure factor of the metal respectively.

The computed results using two sets of eigenvalues have been presented in TABLE 2 alongwith the experimental data for comparison. The form factor of Mg and Ca have been presented in figure 1 and 2 respectively for inspection.

Knight shift

The Knight shift (K%) has been computed through the Pake formula[12] given by,

$$\frac{K_1}{K_0} = -\frac{3Z}{4E_F k_F^2}\int_0^\infty a(q)w(k,q)\ln\left|\frac{q+2k_F}{q-2k_F}\right| dq \qquad (3)$$

where E_F is the Fermi energy of the metal and K_0 is the single OPW value of the Knight shift of the metal.

The form factors yielding better agreement of the electrical resistivity have been used to compute the Knight shift of the metals under investigation. The computed result has been presented in TABLE 3.

Findings

A perusal of the figure 1 and figure 2 reveals that the computed form factors w(k,q) have been significantly affected by the choice of eigenvalues specially in the region of η>1 which is the most contributing region of the Ziman and Pake integrands. This is due to the fact that the first peak of the structure factor a(q) lies in this region.

TABLE 2 shows the computed electrical resistivities of the metals Mg and Ca. For Mg the C eigen values and for Ca the H eigenvalues gives better agreement with experiment. As the electrical resistivity is a property which is fairly sensitive to the nature and magnitude of the form factor is used as a test of the propriety of the form factor itself.

The selected form factors have been used to compute the Knight shift (K%) presented in TABLE 3. For Mg reasonable agreement has been obtained. However, for Ca the experimental data is not available for comparison.

CONCLUSION

From the above study it may be concluded that the HFP pseudopotential technique is fairly successful in predicting the transport properties of alkaline earth metals provided suitable choice of core energy eivenvalues is made.

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