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A COMPARATIVE STUDY OF BAND STRUCTURE ENERGY OF Li, Na, & K LIQUID ALKALI METALS

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ABSTRACT

Band structure energy of Li, Na & K liquid alkali metals have been studied using Harrison's first principle pseudopotential approach. It has been suitably modified as per Moriarity approach. The first principle method gives unifomly good agreement of band structure energy for these alkali metals.

Key words: Mean free path, Fermi surface-, Free electron energy, Band structure energy, Hartee energy, Electrostatic Energy.

INTRODUCTION

In case of liquid alkali metals Li, Na and K the mean free path of an electron may be too large in comparison to the range of correlation of the ions. The disorder scattering will tend to blur the Fermi surface. The self consistent field approximation is better in discussing the electronic states in metals, because in this approximation we have an advantage of considering the effect of the interaction of given electron with all others by potentials, which is the function of Schrodinger equation.

Here we focus our attention on the band structure energy depending up on interaction between atoms. The various properties can be evaluated from total energy depending on ionic co-ordinate. In alkali metals, (Li, Na & K), long-range forces arise from interaction between ions modulated by conduction electrons. The origin of these forces may be seen from the Friedal oscillation[1],[2,3] [Phil. Mag. 43, 153 (1952), Adv. Phys. 3, 446 (1954), Buovo Cimento 2, 287 (1958)] in the screening field. Such fluctuating charge densities arising from one atom must inevitably lead to fluctuating forces on atoms at large distance. In ionic crystal the coulomb interaction between atoms extends for large distances.

Formulation

The total energy of crystal is consisted, of two contribution:

(a) Free electron energy (E_{fe})

This energy depends on total volume but is independent of ionic co-ordinates.

(b) Band structure energy (E_{bs})

This energy depends on ionic configuration. Within the frame work of pseudopotential perturbation theory the expression for electron energy is given by:

$$E_k = \frac{h^2K^2}{2m} + N \langle \underline{K} + \underline{q} \mid w \mid \underline{k} \rangle + N^2 \sum_{q}' S^*_g(q)\, S_q(q) + \frac{\langle \underline{k+q} \mid w \mid \underline{k} \rangle \langle \underline{k} \mid w \mid \underline{k+q} \rangle}{E_k - E_{k+q}} \quad \ldots\ldots\ldots\ldots\ldots(1)$$

The prime on the summation over q indicates K, q, q=0 terms is to be excluded.

The total energy per ion in metal which includes the electron energy plus the direct ion-ion interaction, the electron ion interaction and correlation interaction between electrons may be written as.

$$E = (2N)^{-1} \sum_{i \neq j} \frac{z^2 e^2}{|R_i - R_j|} + (N)^{-1} \sum_{k < k_F} \langle \Psi_k | T + V_c | \Psi_k \rangle$$

$$-(N)^{-1} \int \frac{P_e(r)\, P_c(r)}{|r - r'|}\, d^3 r\, d^3 r'$$

$$+ (N)^{-1} \int P(r) \{E_{axch} Pc(r) - \mu_{axch} Pc(r)\}\, d^3 r' \quad \ldots\ldots\ldots\ldots(2)$$

Where N is the number of ion. T is the kinetic energy, V_c is the crystal potential which contains coulomb, exchange and correlation interactions of electrons, $P_c(r)$ is the charge density of the conduction electrons, μ_{axch} $P_c(r)$ and E_{exch} $P_c(r)$.are the exchange and correlation chemical potential and energy per electron respectively. The electrostatic interaction between the ions are added and we subtract an energy equal to the electron - electron interaction. We consider four charge densities.

/ (i) Charge density due to valence charge of the nuclei (val)

/ (ii) Charge density due to the orthogonalization holes (hole)

(iii) Charge density due to the uniform background compensating these two (unit) and

(iv) The screening charge density (scr). The negative of the electrostatic energy of the conduction electrons interacting with themselves as-

-1/2 (unif+ hole+ scr) (unif +hole+ scr). The energy of the valence charges interacting with each other as

1/2 (val)(val)'

Where the prime indicates that terms involving interaction of a given nucleus with itself are to be omitted. The contribution of <k | w | k > to the total energy is obtained by summing over occupied electron states, <k | w | k >may be rewritten as

$$\langle k|w|k\rangle = \langle k|V|k\rangle + \sum_{\alpha} (h^2k^2/2m + \langle k|V|k\rangle - E_\alpha) \times \frac{\langle k|\alpha\rangle\langle\alpha|k\rangle}{1 - \langle k|P|k\rangle} \quad \ldots\ldots\ldots(3)$$

The total contribution of <k | V | k > is simply N Z V; again N is the_number of ions present, Z the valence, and V is the average of the potential. V is given by

$$\bar{V} = V_o^c + V_o^d + 1/(NZ^*)(unif)\{(Z^*/Z)(val) + (unif)\} \quad \ldots\ldots\ldots(4)$$

Now E_α is given by.

$$E_\alpha = -|\in_1| + V_{opw} - (1/NZ)(val) \times \{(Z^*/Z)(val)' + (unif) + (scr)\}. \quad \ldots\ldots\ldots(5)$$

Where - | G j is Hartree energy for free ion. Hence eq.(3) may be written as

$$\langle k|w|k\rangle V_o^c + V_o^d + 1/(NZ^*)(unif)\{(Z^*/Z)(val) + (unif)\} + \sum_{\alpha} \{(h^2k^2/2m + V_o^c + V_o^d + |\in_f| + -V_{opw})\}$$

$$+1/NZ^*\{(Z^*/Z)(val)+(unif)\}\{(Z^*/Z)(val)+(unif)+(scr)\} \times \frac{\langle k|\alpha\rangle\langle\alpha|k\rangle}{1 - \langle k|P|k\rangle} \quad \ldots\ldots\ldots(6)$$

The contribution to the total energy is given by summing the last term of equ (6) over all electrons.

i.e, .

$$\frac{1}{N}\sum_{\kappa}\sum_{\alpha}\frac{\langle k|\alpha\rangle\langle\alpha|k\rangle}{1-\langle k|P|k\rangle} = \frac{1}{N}\sum_{\kappa}\sum_{t}\frac{\langle k|t\rangle\langle t|k\rangle}{1-\langle k|P|k\rangle} = Z^* - Z$$

The total contribution to the energy of$\langle k|w|k\rangle$ and the two electrostatic terms is then.

$$NZ^* = (V_o^c+V_o^d) + N\sum_k\sum_t \frac{h^2k^2}{2m} + |\in_1| - (V_{opw})\frac{\langle k|t\rangle\langle t|k\rangle}{1-\langle k|P|w\rangle} + \text{+Z/Z* (unif)\{(Z/Z)(val)+ (unif)\} +\{(Z*-Z)/Z*\}\{Z*/Z(val) +(unif)\} x \{Z*/Z (val) +(unif) +(scr)\} +½(Val)(Val)}^{-1} \text{– ½\{(unif) +(hole) +(scr)\} (unif +hole+ scr)} \quad \text{.....(7)}$$

The electrostatie energy of the hole on a given ion with its own potential is ½ (Z* - Z)V_{opw} -%(hole)(hole)= %(Z*-Z)/Z, (val)(val)-^{1} +N/2 (Z*-Z) V_{opw}

.....(8)

We may replace (hole) by z*-z)/z(val).

After reassembling terms in equ. (7) we obtain without further approximation.

$$NZ^* = (V_o^c+V_o^d) + \sum_k\sum_t \frac{h^2k^2}{2m} + |\in_1| - (V_{opw}/2)\frac{\langle k|t\rangle\langle t|k\rangle}{1-\langle k|P|k\rangle} \text{ -½(scr)(scr) +½\{Z*/Z(val)+(unif)\}\{Z*/Z(val) +unif)\}}^{-1} \quad \text{.....(9)}$$

The total kinetic energy,(3/5)NZ $h^2k^2_F$/2m is added to the first, two contributions of equ.(9) to give the free -electron energy. The resultant energy ion is

$$E_{fe} = 3/5\ Z\ h^2k^2_F/2m + Z^*(V_0^c+V_0^d) + \frac{1}{N}\sum_{kt}\frac{h^2k^2}{2m} + |\in_t| - (V_{opw}/2)\frac{\langle k|t\rangle\langle t|k\rangle}{1-\langle k|P|k\rangle} \quad \text{.....(10)}$$

The first contribution in equ.(9) in the electrostatic energy of point ions of charge Z* exbedded in a uniform compensatory background,This is the electrostatic energy, or the direct interaction between ions.

The electron energy may be rewritten using the factored form of the matrix elements as

$$E(k) = \frac{h^2k^2}{2m} + \langle k|w|k\rangle + \sum_q^1 \frac{S^*(q)\,S(q)\langle k|w|k+q\rangle\langle k+q|w|k\rangle}{(h^2/2m)(k^2-|k+q|^2)} \quad \text{.....(11)}$$

For expressing the contribution otthe third term in equation (10) we interchange the summation over q and the interaction over k to obtain the form

$$\sum S^*(q)S(q)\frac{2\Omega_0}{(2\pi)^3} = \int \frac{\langle k|w|k+q\rangle\langle k+q|w|k\rangle}{(h^2/2m)(k^2-|k+q|^2)}$$

The expression to the right of S* (q) S(q) is a function of wave number q. The function is determined entirely by local potentials and volume of the system through the wave number K_F. Furthermore, because of the spherical symmetry of local potentials, this is a function of the magnitude of q only. Now the function is called the energy wave number characteristic and written as F(q).

The second contribution to the energy per ion comes from the final term in the electron energy. It is called the bands-structure energy and may be written as

$$E_{bs} = \sum_q^1 S^*(q)\,S(q)\,F(q) \quad \text{.....(12)}$$

Where

$$F(q) = \frac{2\Omega_0}{(2\pi)^3} \int d^3k \frac{\langle k+q| w |k\rangle^2}{(h^2/2m)(k^2 - |k+q|^2)} \frac{q^2\Omega_0}{8\pi e^3}$$

$$|V_q^{scr}|^2 \quad \text{.....(13)}$$

$$V_q^{scr} = (V_q^{ab} + V_q^{c} + V_q^{d})\{1 - \in(q)\}/\in(q) + V_q^{l}/\in(q) \quad \text{.....(14)}$$

$$F(q) = \frac{\Omega_0 K_F^2}{4\pi^2 q^2} \int_{-1}^{+1} \frac{dZ}{2Z + q/k_F} \int_0^{\sqrt{1-Z}} dp\, 2p\, |\langle k+q| w |k\rangle|^2$$

$$- \frac{q^2\Omega_0}{16\pi} (V_q^{scr})^2 \quad \text{.....(15)}$$

For liquid S* (q) S (q) is a function of only the magnitude of q. Hence summation in equ. (12) is written as an integral,

$$E_{bs} = \frac{\Omega_0}{(2\pi)^3} \int_0^{\infty} dq\, 4\pi q^2\, S^*(q)\, S(q)\, F(q) \quad \text{.....(16)}$$

Using the property $N|S(q)|^2 = a(q)$; the equation (16) transforms into

$$E_{bs} = \frac{3Z}{2K_F^3} \int_0^{\infty} q^2\, a(q)\, F^*(q)\, dq \quad \text{.....(17)}$$

Table -1 : The Band Structure Energy (in Ryd.) of Li, Na and K Liquid Alkali Metals

Metal	Melting point in (K)	(Eba)cal	$(E_{ba})_H$	(Eba)AH
Li	453	0.143	-0.052	-0.152
Na	373	0.067	-0.076	-0.014
K	343	0.090	-0.087	-0.013

Using the different forms of dielectric functions and Equ. (15) of energy wave -number - characteristic function F(q), the band structure energy of liquid alkali metals have been evaluated from Equ. (17). For liquid structure factor a(q) we have used experimental structure factor.

The obtained results of band structure energy of Li, Na and K liquid alkali metals are listed in Table-1 and are compared with other theoretical results.

RESULTS

Table (1) presents the computed values of band structure energy of alkali metals (Li, Na, & K). It is found that the first principle method gives uniformly good agreement of band structure energy for lithium, sodium & potassium.

CONCLUSION

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In order to study the band structure by using Harrison's first principle pseudopotential approach[4] [Pseudopotential in the theory of metal's (W.A. Benjamin, Inc New York, 1966)] has to be suitably modified[5,6] like Moriarty [Phys.FSev. B-1, 1363 (1970), Phys. Rev. B-6, 1239 (1972)] approach.

It is found that taking into the account the modifications suggested the calculated band structure energies of liquid alkali metals (Li, Na, & K) agree well with the observed value for the same in the literature.

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