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STUDY OF BAND STRUCTURE OF ENERGY OF LIQUID ALKALI METALS (Li, Na, K, Rb and Cs)

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ABSTRACT

Band structure of energy of liquid alkali metals has been presented. In the structure of the theory the important in gradients are the form factors and the structure factors. As the approach rests heavily on the assumption that the potential is considerable weak. The alkali metals have been favourite of theoretical account of their simple free electron like nature band structure study and Fermi surface measurements. The discrepancy in the computed results can also be attributed to the neglect of various harmonic effects such as multiphonon processes and partially due to magnitude of form factors and energy wave number characteristic. The various properties can be evaluated from total energy depending on ionic co-ordinate.

Key words: Band structures, Ionic co-ordinate, Fermi surface.

INTRODUCTION

In case of liquid metal the mean free path of an electron may be too large compared to the range of correlation of the ions and 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 will all others by potentials, which is then function of Schrodinger equation.

In this study, we focused our attention on the band structure energy depending upon interaction between atoms the various properties can be evaluated from total energy depending on ionic co-ordinate. In alkali metals (Li, Na, K, Rb and Cs) long range force arise from interaction between ions modulated by conduction electrons. The origin of these forces may be seen from the Friedal oscillation[1-3] in the screening field. Such fluctuation charge densities arising from one atom must inevitably lead to fluctuating forces on atoms at

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large distance. In ionic crystal the coulomb interaction between atoms extends of course for large distances.

EXPERIMENTAL

Mathematical formulation

The total energy of a 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. With in the frame work of pseudopotential perturbation theory the expression for electron energy is given by -

$$\mathrm{Ek} = \frac{\mathrm{h}_2\,\mathrm{k}_2}{2\,\mathrm{m}} + N(\underline{K}+\underline{q}\,|\,\mathrm{w}\,|\,\underline{k}) + N^2 \sum_{q}^{1} S^*{}_g\,(q)\,S_q\,(q)$$

$$+\ \frac{(\underline{K}+\underline{q}\,|\,\mathrm{w}\,|\,\underline{k})\ (\underline{K}\,|\,\mathrm{w}\,|\,\underline{k}+\underline{q})}{E_k - E_{k-a}} \qquad \ldots(1)$$

The prime on the summation over q indicates K_q q = O terms is to be excluded.

Hence the total energy per ion in metal which includes the electron energy plus the direct ion-ion interaction, the electron ion interaction and correlation between electrons can be written as –

$$\mathrm{E} = (2\mathrm{N})^{-1}\,\Sigma = \frac{\mathrm{Z}^2\mathrm{e}^2}{\mathrm{i} \neq \mathrm{j}\,|\,\mathrm{R}_\mathrm{i} - \mathrm{R}_\mathrm{j}\,|} + (\mathrm{N}) - 1 \sum_{\mathrm{k}<\mathrm{kf}} (\psi_\mathrm{k}\,|\,\mathrm{T} + \mathrm{Vc}\,|\,\psi_\mathrm{k})$$

$$(\mathrm{N})^{-1} f\ \frac{\mathrm{Pe\,(r)\,Pc\,(r)}}{|\,\mathrm{r} - \mathrm{r}'\,|} + \mathrm{d}^3\,\mathrm{r}\,\mathrm{d}^3\,\mathrm{r}' \qquad \ldots(2)$$

$$+\ (\mathrm{N})^{-1} f\ \mathrm{pe\,(r)}\ [\mathrm{E}_{\mathrm{exch}}\,\mathrm{Pe\,(r)} - {}_{\mu\mathrm{exch}}\,\mathrm{Pe\,(r)}\,\mathrm{d}^3\,\mathrm{r}'$$

Where N is the number of ion. T is the kinetic energy Vc is the crystal potential which contains coulomb, exchange and correlation interactions of electrons. Pc (r) the charge density of the conduction electorns. $_{\mu exch}$ Pe (r) and E_{exch} Pe (r) are the exchange and correlation chemical potential and energy per electron, respectively. The electrostatic interaction between the ions is 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 (unif) and

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

$$-1/2 \text{ (unit + hole + scr) unif + hole + scr}$$

The energy of the valence charge interacting with each other as -

$$\tfrac{1}{2} \text{ (val) (val)}$$

Where the prime indicates that terms involving interaction of a given nucleus with itself are to be omitted. The contribution of $(k \mid w \mid k)$ to the total energy is obtained by summing over occupied electron states. $(k \mid w \mid k)$ may be written as -

$$(k \mid w \mid k)\ (k \mid V \mid k) + \Sigma_\alpha (h^2 k^2 / 2m + (k \mid V \mid k) - E\ \alpha)\ \text{x}\ \frac{(k \mid \alpha \mid)\ (\alpha \mid k)}{1\text{-}(k \mid P \mid k)} \qquad \ldots(3)$$

The total contribution of $(k \mid V \mid k)$ is simply NZV again N is the number of ions present. Z the valence. And V is the average of the potential. V is given by

$$V = V_0^C + V_0^d + (1/N\ Z^*)\ (\text{unif})\ (Z^*/Z)\ (\text{val}) + (\text{unif})] \qquad \ldots(4)$$

Now E_t is given by -

$$E_t = \mid 1 \mid + \text{Vopw} - (1/N\ Z^*)\ \text{val})\ \text{x}\ [(Z^*/Z)\ (\text{val})' + {}^*\text{unif}) + (\text{scr})] \qquad \ldots(5)$$

Where $- \mid\ \mid$ is hartee energy for free ion. Hence Eq. (3) may be rewritten as -

$$[(k\ l\ w\ l\ k) = V_o^c + V_o^d + (1/N\ Z^*)]\ (\text{unif})\ [(Z^*/Z)\ (\text{val}) + (\text{unif})]$$

$$+ \Sigma_\alpha [(h^2 + k^2/2m) + V_0^c + V_0^d + l \in_l l - \text{Vopw}]$$

$$+ (1/NZ^*)\ [(Z^*/Z)\ (\text{val}) + (\text{unif})\ [(Z^*/ Z)\ (\text{val}) + (\text{unif}) + (\text{scr})$$

$$\text{x}\ \frac{(k \mid \alpha)\ (\alpha \mid k)}{1\text{-}(k \mid P \mid k)} \qquad \ldots(6)$$

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

$$\frac{1}{\mathrm{N}}\sum_k \sum_\alpha \frac{(\mathrm{k}\,|\,\alpha)\,(\alpha\,|\,\mathrm{k})}{1-(\mathrm{k}\,|\,\mathrm{P}\,|\,\mathrm{k})}$$

$$= \frac{1}{\mathrm{N}}\sum_k \sum_\alpha \frac{(\mathrm{k}\,|\,\mathrm{t})\,(\mathrm{t}\,|\,\mathrm{k})}{1-(\mathrm{k}\,|\,\mathrm{P}\,|\,\mathrm{k})}$$

$$= \mathrm{Z}^* - \mathrm{Z}$$

The total contribution to the energy of (k | w | k) and the two electrostatic terms is then.

$$\mathrm{NZ}^*\,(\mathrm{V}_0^{\mathrm{c}} + \mathrm{V}_0^{\mathrm{d}}) + \mathrm{N}\,\Sigma_{\mathrm{x}}\,\Sigma_\alpha\,\frac{\mathrm{h}_2\,\mathrm{k}_2}{2\,\mathrm{m}}\;|\in_1|-\mathrm{V}_{\mathrm{opw}}]\;\frac{(\mathrm{k}\,|\,\mathrm{t})\,(\mathrm{t}\,|\,\mathrm{k})}{1-(\mathrm{k}\,|\,\mathrm{P}\,|\,\mathrm{k})}$$

$$+\;\frac{(\mathrm{Z}^*\,\mathrm{Z})}{\mathrm{Z}^*}\;\left(\frac{\mathrm{Z}^*}{\mathrm{Z}}(val)+(unif)\right.][\left(\frac{\mathrm{Z}^*}{\mathrm{Z}}(val)+(unif)+(scr)\right.]$$

$$+\;(1/2)\,(\mathrm{val})\,(\mathrm{Val})^{-1} - (1/2)\,[(\mathrm{unif}) + (\mathrm{hole}) + (\mathrm{scr})]$$

$$(\mathrm{unif} + \mathrm{hole} + \mathrm{scr}) \qquad \ldots(7)$$

The electrostatic energy of the hole on a given ion with its own potential is ½ (Z^* - Z) V opw.

$$-\;\frac{1}{\mathrm{Z}^*}\;\frac{(hole)\,(hole)}{Z} = \frac{1}{2}\;\frac{(\mathrm{Z}^*\,\mathrm{Z})}{\mathrm{Z}^*},\;(\mathrm{val})\,(\mathrm{val})\;\text{-}1 = \frac{\mathrm{N}}{2}\,(\mathrm{Z}^*\,\mathrm{Z})\,\mathrm{V}_{\mathrm{opw}} \qquad \ldots(8)$$

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

After reassembling terms in Eq. (7) We obtain without further approximation.

$$\mathrm{NZ}^*\,(\mathrm{V}_{\mathrm{o}}^{\mathrm{c}} + \mathrm{V}_{\mathrm{o}}^{\mathrm{d}}) + \Sigma_{\mathrm{x}}\,\Sigma_\alpha\,\frac{\mathrm{h}_2\,\mathrm{k}_2}{2\,\mathrm{m}}\;1\in_1 1-(\mathrm{V}_{\mathrm{opw}}\,/\,2)\;\frac{(\mathrm{k}\,|\,\mathrm{t})\,(\mathrm{t}\,|\,\mathrm{k})}{1-(\mathrm{k}\,|\,\mathrm{P}\,|\,\mathrm{k})}$$

$$-\;\frac{1}{2}\,(\mathrm{scr})\,(\mathrm{scr}) + \frac{1}{2}\;\frac{(\mathrm{Z}^*)}{\mathrm{Z}},\;(\mathrm{val})\,(\mathrm{val})\left(\frac{\mathrm{Z}^*}{\mathrm{Z}}\,(\mathrm{val})\,(\mathrm{unif})\right. \qquad \ldots(9)$$

The total kinetic energy, (3/5) N Z h^2 k^2/ 2m is added to the first two contributions of Eq. (9) to five the free electron energy the resultant energy per ion is

$$\text{Eye } 3/5\, Z\, (h^2\, k^2 / 2m) + Z^*\, (V_o^c + V_o^d)$$

$$\pm \frac{1}{N} \Sigma_{k\text{-}f} \frac{h_2\, k_2}{2\,m} + |\, \in_1 \,| - V_{opw} / 2]\; \frac{(k\,|\,t)\,(t\,|\,k)}{1\text{-}\,(k\,|\,P\,|\,k)} \qquad \ldots(10)$$

Using the different forms of dielectric functions and Eq. of energy wave number characteristic function F (q) the band structure energy of liquid alkali metals have been for liquid structure factor q (q) we have used experimental structure

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

Table 1: The band structure energy (in Ryd) of liquid alkali metals

Metal	**Melting point in (K)**	**(E_{bs}) Cai**		
Li	453	0.144	-0.053	-0.153
Na	373	0.068	-0.077	-0.015
K	343	0.091	-0.088	-0.014
Rb	313	0.012	-0.128	-0.015
Cs	303	0.242	-0.164	-0.016

$(E_{bs})_{ss}$ = Band structure energy calculated from scheider- St II model

$(E_{bs})_{AH}$ = Band structure energy calculated from Animalu-Heine model

RESULTS AND DISCUSSION

Table 1 presents the computed value of band structure energy of alkali metals (Li, Na, K, Rb and Cs). It is found that the first principle method gives uniformly good agreement of band structure energy for lithium. Sodium potassium and rubidium. In the case of cesium the picture is poor.

Such a case may arise on account of the d-level effect. The discrepancy in the computed results can also be attributed to the neglect of various harmonic effect such as multiphonon processes and partially due to magnitude of form factors and energy wave number characteristics.

CONCLUSION

- In order to study the band structure by using Harrison's first principle pseudo potential approach has to be suitably modified like moriarty.
- A correct term on account of spin orbit coupling for heavy metals like cesium may also be needed in the band structure energy expression.
- In view of the above we expect that a good agreement is possible in case of Li, Na, K and Rb with minor disagreement in case of Na and major disagreement in the case of Cs.

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