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STATIC AND VIBRATIONAL PROPERTIES OF LITHIUM ALLOYS

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The computations of the static and vibrational properties of four equiatomic lithium alloys viz. $\text{Li}_{0.5}\text{Na}_{0.5}$, $\text{Li}_{0.5}\text{K}_{0.5}$, $\text{Li}_{0.5}\text{Rb}_{0.5}$ and $\text{Li}_{0.5}\text{Cs}_{0.5}$ to second order in local model potential is discussed in terms of real-space sum of Born von Karman central force constants. The local field correlation functions due to Hartree (H), Ichimaru-Utsumi (IU) and Sarkar et al. (S) are used to investigate influence of the screening effects on the aforesaid properties. Results for the lattice constants i.e. C_{11} , C_{12} , C_{44} , $C_{12} - C_{44}$, C_{12}/C_{44} and bulk modulus \bar{A} obtained using the Hartree (H) local field correction function has higher values in comparison with the results obtained for the same properties using Ichimaru-Utsumi (IU) and Sarkar et al. (S) local field correction functions. The results for the Shear modulus (C'), deviation from Cauchy's relation, Poisson's ratio σ , Young modulus Y , propagation velocity of elastic waves, phonon dispersion curves and degree of anisotropy A are highly appreciable for the four lithium alloys.

Keywords: PHONON DISPERSION CURVES, LITHIUM ALLOYS,
PSEUDOPOTENTIAL, LOCAL FIELD CORRECTION FUNCTION.

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1. INTRODUCTION

In the study of various properties of solids, one frequently requires the knowledge of interaction energy between the ions or atoms. The study of a pair effective interionic interaction in simple metals has a long history and originally they were not systematized and were concerned with individual groups of metals. In recent years considerable attention has been devoted to the theoretical study of the nature of effective interaction between constituent atom or ion in simple metals [1-14]. The bcc $A_{1-x}B_x$ ($A = \text{Li}$; $B = \text{Na, K, Rb, Cs}$) alloy system forms substitutional solid solution overall region of concentration x of the second component and the crystal binding of the solid solution is unchanged compared with that of the pure alkali metals. Theoretical studies about the lattice dynamics of the alloy systems have been devoted to $\text{Li}_{0.5}\text{Na}_{0.5}$, $\text{Li}_{0.5}\text{K}_{0.5}$, $\text{Li}_{0.5}\text{Rb}_{0.5}$ and $\text{Li}_{0.5}\text{Cs}_{0.5}$ systems since the lattice dynamics of the pure alkalis has been investigated in detail. But the work on the comprehensive study of static and vibrational properties alkali binary alloys is almost negligible [1-14]. Only Soma et al. [12] have studied the phonon dispersion curves of $\text{Cs}_{0.7}\text{K}_{0.3}$, $\text{Cs}_{0.7}\text{Rb}_{0.3}$,

$\text{Cs}_{0.3}\text{Rb}_{0.7}$ and $\text{Rb}_{0.71}\text{Cs}_{0.29}$ alloys. Vora and co-workers [1-6] have reported the static and vibrational properties of equiatomic lithium based binary alloys using model potential formalism. Recently, Gajjar et al. [7] have studied the lattice dynamics of bcc $\text{Cs}_{0.3}\text{K}_{0.7}$ alloy. Experimentally, Kamitakahara and Copley [13] have studied the lattice dynamics of $\text{Rb}_{1-x}\text{K}_x$ alloys with $x = 0.06, 0.18$ and 0.29 by neutron scattering. Recently, Chushak and Baumketner [9] have reported the dynamical properties of liquid $\text{Cs}_{0.3}\text{K}_{0.7}$ alloy. Hence, we have decided to work on four equiatomic lithium based binary alloys i.e. $\text{Li}_{0.5}\text{Na}_{0.5}$, $\text{Li}_{0.5}\text{K}_{0.5}$, $\text{Li}_{0.5}\text{Rb}_{0.5}$ and $\text{Li}_{0.5}\text{Cs}_{0.5}$. Well known single parametric local model potential of Gajjar et al. [1-7] is used to describe the electron-ion interaction. For the first time an advanced and more recent local field correlation functions due to Ichimaru-Utsumi (IU) [15] and Sarkar et al. [16] has been employed in such investigations. This helps in identifying the influence of exchange and correlation effects in the static form of Hartree (H) (only static) dielectric function [17].

2. THEORETICAL METHODOLOGY

The phonon frequencies can be obtained by solving the standard secular determinantal equation [1-9]

$$\det \left| D_{\alpha\beta}(q) - 4\pi^2 v^2 M \delta_{\alpha\beta} \right| = 0, \quad (1)$$

where, M is the ionic mass, v is the phonon frequency and $D_{\alpha\beta}(q)$ is the dynamical matrix in which the force between two ions depends only upon the distance between them is given by,

$$D_{\alpha\beta}(q) = \sum_n \left(1 - e^{iqr} \right) \left. \frac{d^2 \Phi(r)}{dr_\alpha dr_\beta} \right|_{r=r_n}, \quad (2)$$

here $\Phi(r)$ is the interionic pair potential, r_α and r_β are α^{th} and β^{th} Cartesian components of the position vector of n^{th} ion, respectively.

This dynamical matrix element used in the present calculation finally takes the form,

$$D_{\alpha\beta}(q) = \sum_n \left(1 - e^{iqr} \right) \left[K_t + \frac{r_\alpha r_\beta}{r^2} (K_r - K_t) \right], \quad (3)$$

Here K_t and K_r are the force constants between a pair of ions interacting through a central interaction and n specifies shell index.

$$\begin{aligned} K_t &= \frac{1}{r} \frac{d\Phi(r)}{dr} \\ &= -\frac{Z^2 e^2}{r^3} + \frac{\Omega_0}{\pi^2 r^2} \int_0^\infty F(q) q^2 \left[\cos(qr) - \frac{\sin(qr)}{qr} \right] dq. \end{aligned} \quad (4)$$

$$\begin{aligned}
 K_r &= \frac{d^2\Phi}{dr^2} \\
 &= \frac{2Ze^2}{r^3} + \frac{\Omega_0}{\pi^2 r^2} \int_0^\infty F(q) q^2 \left[\frac{2\sin(qr)}{qr} - 2\cos(qr) - qr\sin(qr) \right] dq, \quad (5)
 \end{aligned}$$

where $F(q)$ is the energy wave number characteristic given by [1-9]

$$F(q) = \frac{\Omega_0 q^2}{8\pi e^2} |W_B(q)|^2 \frac{[\varepsilon_H(q) - 1]}{1 + [\varepsilon_H(q) - 1][1 - f(q)]}, \quad (6)$$

with Ω_0 , $W_B(q)$, $\varepsilon_H(q)$ and $f(q)$ are the atomic volume, bare-ion pseudopotential, static Hartree dielectric function and local field correlation function, respectively.

The bare-ion pseudopotential due to Gajjar et al. [1-7] is given by

$$W_B(q) = \frac{-8\pi Z}{\Omega_0 q^2} \left(\cos(qr_C) - \frac{(qr_C)^2}{1 + (qr_C)^2} \right), \quad (7)$$

here, Z and r_C are the valence and parameter of the model potential, respectively. The details of the model potential are narrated in the literature [1-7].

Using these atomic force constants, we can generate inter atomic force constants $K_{\alpha\beta}$ which can then be employed to investigate the elastic constants,

$$\begin{aligned}
 K_{\alpha\beta} &= \frac{d^2\Phi(r)}{dr_\alpha dr_\beta} \\
 &= \left[\delta_{\alpha\beta} - \frac{r_\alpha r_\beta}{r^2} \right] K_t + \frac{r_\alpha r_\beta}{r^2} K_r. \quad (8)
 \end{aligned}$$

Under the long-wave phonon method, the lattice constants i.e. $C_{11}, C_{12}, C_{44}, C_{12} - C_{44}$, Cauchy's ratio C_{12} / C_{44} , shear modulus C' , bulk modulus B , Poisson's ratio σ , Young modulus Y , propagation velocity of longitudinal and transverse waves in [100], [110] and [111] directions, behavior of phonon frequencies in the limit independent of direction and degree of elastic anisotropy A are computed from the well known relations [1-9].

3. RESULTS AND DISCUSSION

The constants and parameters employed for the present computational study are listed in Table 1. In evaluating integration in Eqs. (4) and (5) the upper limit of integral is taken $40 k_F$ so that, a complete convergence of the model potential is achieved at higher momentum transfer and it covers all the oscillations of the form factor. Therefore, any artificial / fictitious cut-off in the present computations is avoided. In the present computation the error associated will be of the order of $10^{-6} k_F / 2$. We have performed the real space sum analysis up to 33 sets of nearest neighbours in r -space, which are

found sufficient for computing the elastic constants and bulk modulus using interatomic force constants, to consider a long-range character for proper convergence of the calculation and to achieve desired accuracy. The present model is valid for both ordered and disordered alloys [1-7].

Table 1 – Constants and parameters for equiatomic lithium based binary alloys

Metal	Z	k_F (au)	Ω_0 (au) ³	r_C (au)
Li	1	0.5890	144.9	0.7738
Na	1	0.4882	254.5	1.0765
K	1	0.3947	481.4	1.3880
Rb	1	0.3693	587.9	1.4837
Cs	1	0.3412	745.5	1.9108

In the present computation, the bcc crystal structure considered for all the solid solutions. The lattice constants ‘ a ’ are obtained from the well known relation $(2\Omega_0)^{1/3}$. Table 2 displays the computed values of some static and vibrational properties of four equiatomic lithium based binary alloys. It is noted from the Table 2 that, our results calculated for C_{11} , C_{12} , C_{44} , $C_{12} - C_{44}$, C_{12} / C_{44} and bulk modulus B from H-local field correction function give higher values than those obtained for the IU and S-local field correction functions. There is a good agreement for the calculated values of the Shear modulus C' , deviation from Cauchy’s relation, Poisson’s ratio σ , Young modulus Y , propagation velocity of elastic waves, phonon dispersion curves (PDC) and degree of anisotropy A using H, IU and S-local field correction functions.

It is noticed from the present study that, the percentile influence of the IU-local field correction function with respect to the static H-local field correction function on the vibrational properties of $\text{Li}_{0.5}\text{Na}_{0.5}$, $\text{Li}_{0.5}\text{K}_{0.5}$, $\text{Li}_{0.5}\text{Rb}_{0.5}$ and $\text{Li}_{0.5}\text{Cs}_{0.5}$ is found 0 % – 70.42 %, 0.78 % – 79.23 %, 3.75 % – 50.68% and 1.76 % – 63.53 %, respectively. Such influence of the S- local field correction function with respect to the static H-local field correction function on the vibrational properties, for $\text{Li}_{0.5}\text{Na}_{0.5}$ is 0.71 % – 61.58 %, for $\text{Li}_{0.5}\text{K}_{0.5}$ is 0 % – 0.05 %, for $\text{Li}_{0.5}\text{Rb}_{0.5}$ is 2.08 % – 82.35 % and for $\text{Li}_{0.5}\text{Cs}_{0.5}$ is 2.27 % – 30.29 %. This clearly indicates that the local field correlations play a very effective role in explaining correctly the static and dynamic properties of such solid solutions. Same results of the static and vibrational properties are obtained from H and S-local field correction functions for $\text{Li}_{0.5}\text{K}_{0.5}$ solid solution.

The H-local field correction function [12] is purely static and it does not include the exchange and correlation effects. The IU-local field correction function [10] is a fitting formula for the dielectric local field correction function of the degenerate electron liquids at metallic and lower densities, which accurately reproduces the Monte-Carlo results as well as it also satisfies the self consistency condition in the compressibility sum rule and short range correlations. Therefore, the IU-local field correction function affects the longitudinal phonon branches only. On the basis of IU-local field correction function [10], Sarkar et al. [11] have proposed a simple and analytical form of the local field correction function.

Table 2 – Static and vibrational properties of lithium alloys

Properties	Li _{0.5} Na _{0.5}			Li _{0.5} K _{0.5}			Li _{0.5} Rb _{0.5}			Li _{0.5} Cs _{0.5}		
	H	IU	S	H	IU	S	H	IU	S	H	IU	S
C_{11} in 10^{10} dyne-cm ⁻²	20.63	11.70	13.00	9.75	5.31	9.75	10.98	8.01	4.53	8.01	6.73	5.76
C_{12} in 10^{10} dyne-cm ⁻²	19.44	10.52	11.63	9.21	4.81	9.21	10.26	7.17	4.00	7.33	5.61	5.11
C_{44} in 10^{10} dyne-cm ⁻²	6.65	6.74	6.72	3.53	3.63	3.53	3.63	3.89	2.83	2.99	3.76	2.74
C' in 10^9 dyne-cm ⁻²	5.94	5.90	6.84	2.69	2.55	2.69	3.61	4.21	2.65	3.40	5.56	3.25
B in 10^{10} dyne-cm ⁻²	19.84	10.92	12.09	9.39	4.98	9.39	10.50	7.44	4.18	7.56	5.99	5.32
$(C_{12} - C_{44})$ in 10^{10} dyne-cm ⁻²	12.78	3.78	4.91	5.68	1.18	5.68	6.63	3.27	1.17	4.34	1.86	2.37
Cauchy's ratio (C_{11}/C_{44})	2.92	1.56	1.73	2.61	1.33	2.61	2.82	1.84	1.41	2.45	1.49	1.86
σ	0.49	0.47	0.47	0.49	0.47	0.49	0.48	0.47	0.47	0.48	0.45	0.47
Y in 10^{10} dyne.cm ⁻²	1.77	1.74	2.01	0.80	0.75	0.80	1.07	1.24	0.78	1.00	1.62	0.96
$v_L[100]$ in 10^5 cm-s ⁻¹	4.95	3.73	3.93	3.44	2.54	3.44	2.79	2.38	1.79	2.13	1.95	1.81
$v_T[100]$ in 10^5 cm-s ⁻¹	2.81	2.83	2.83	2.07	2.10	2.07	1.60	1.66	1.42	1.30	1.46	1.25
$v_L[110]$ in 10^5 cm-s ⁻¹	5.63	4.61	4.76	3.97	3.25	3.97	3.17	2.85	2.24	2.46	2.37	2.15
$v_{T1}[110]$ in 10^5 cm-s ⁻¹	2.91	2.83	2.83	2.07	2.10	2.07	1.60	1.66	1.42	1.30	1.46	1.25
$v_{T2}[110]$ in 10^5 cm-s ⁻¹	0.84	0.84	0.90	0.57	0.56	0.57	0.51	0.55	0.43	0.44	0.56	0.43
$v_L[111]$ in 10^5 cm-s ⁻¹	5.85	4.87	5.00	4.14	3.45	4.14	3.29	2.99	2.37	2.56	2.50	2.26
$v_T[111]$ in 10^5 cm-s ⁻¹	1.76	1.77	1.79	1.28	1.29	1.28	1.01	1.06	0.89	0.83	0.96	0.80
Y_1 in 10^{10} dyne-cm ⁻²	4.04	3.00	3.15	20.41	15.25	20.40	12.90	11.17	7.22	7.95	8.09	6.38
Y_2	0.089	0.087	0.10	0.08	0.07	0.08	0.10	0.11	0.09	0.11	0.15	0.12
A	11.20	11.42	9.81	13.11	14.22	13.11	10.05	9.23	10.72	8.81	6.76	8.43

We have also studied the PDC of four equiatomic lithium based binary alloys viz. Li_{0.5}Na_{0.5}, Li_{0.5}K_{0.5}, Li_{0.5}Rb_{0.5} and Li_{0.5}Cs_{0.5} along [100], [110] and [111] directions of high symmetry, which are displayed in Figures 1-4. We have found that the phonon frequencies in the longitudinal branch are more sensitive to the exchange and correlation effects in comparison with the transverse branches. The phonon frequencies in the longitudinal branch are suppressed due to IU-local field correction and enhanced due to S-local field correction functions than the frequencies due to static H-local field correction function. While in the transverse branch, the effects of exchange and correlations enhanced slightly the phonon modes. It is found that at the zone boundaries of [100] and [111] directions of high symmetry, i.e. for the larger momentum transfer the effects of local field correlations are almost negligible. These dispersion curves are not showing any abnormality in the three regions of high symmetry directions and exhibiting qualitative behaviour like metallic elements.

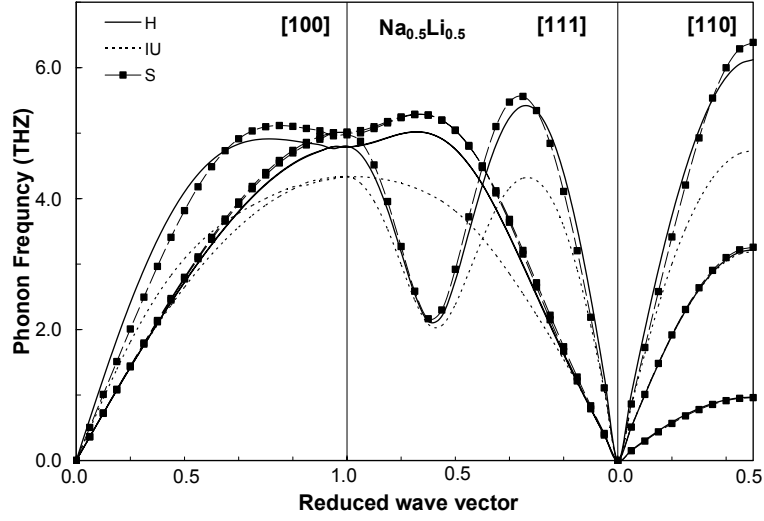


Fig. 1 – Phonon dispersion curves of $\text{Li}_{0.5}\text{Na}_{0.5}$ alloy

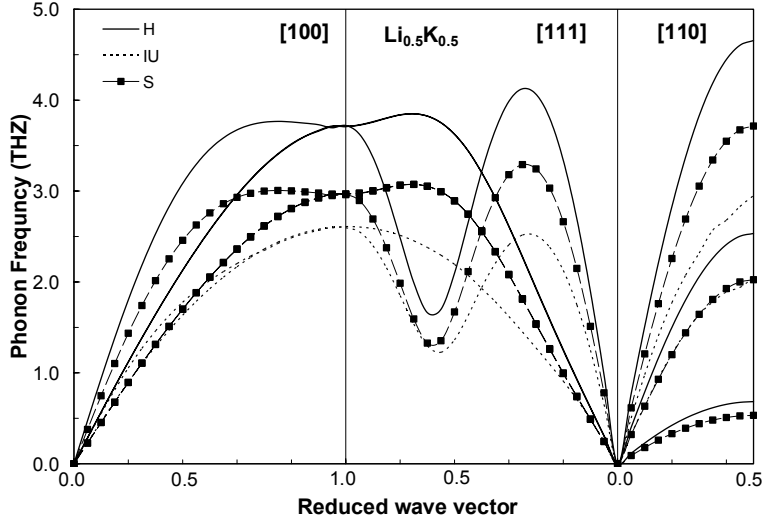


Fig. 2 – Phonon dispersion curves of $\text{Li}_{0.5}\text{K}_{0.5}$ alloy

The phonon frequencies computed from IU-local field correction functions diverged from static H-function in [100] [111] and [100] directions of high symmetry are about 0 % – 91.72 %, 0 % – 42.40 %, 0 % – 21.24 % and 0 % – 34.82 % for $\text{Li}_{0.5}\text{Na}_{0.5}$, $\text{Li}_{0.5}\text{K}_{0.5}$, $\text{Li}_{0.5}\text{Rb}_{0.5}$ and $\text{Li}_{0.5}\text{Cs}_{0.5}$ solid alloys, respectively. While the phonon frequencies computed from S-local field correction functions differed from static H-function in [100], [111] and [100] of high symmetry directions are 0 % – 148.26 % for $\text{Li}_{0.5}\text{Na}_{0.5}$, 0 % – 98.50 % for $\text{Li}_{0.5}\text{K}_{0.5}$, 0 % – 99.19 % for $\text{Li}_{0.5}\text{Rb}_{0.5}$ and 0 % – 99.27 % for $\text{Li}_{0.5}\text{Cs}_{0.5}$ solid solutions.

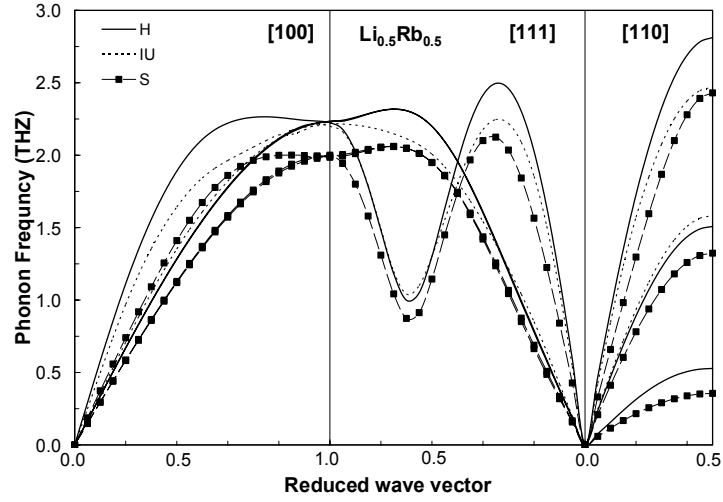


Fig. 3 – Phonon dispersion curves of $\text{Li}_{0.5}\text{Rb}_{0.5}$ alloy

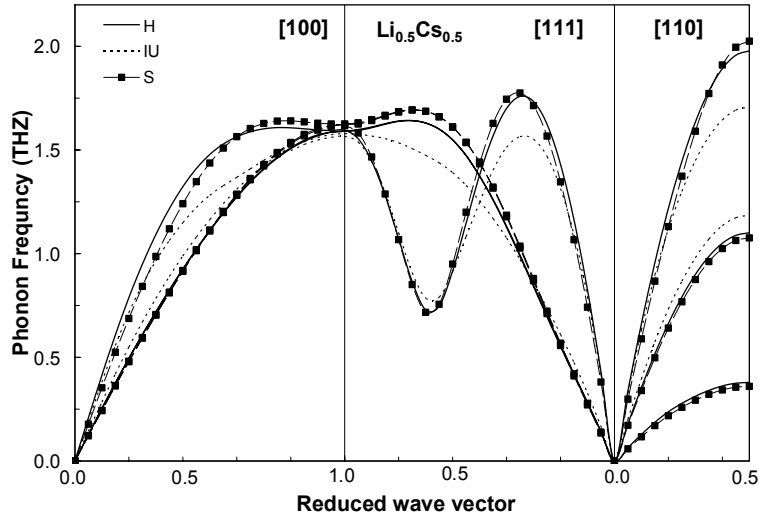


Fig. 4 – Phonon dispersion curves of $\text{Li}_{0.5}\text{Cs}_{0.5}$ alloy

Also, we observed from the PDC that, when we move from $\text{Li}_{0.5}\text{Na}_{0.5} \rightarrow \text{Li}_{0.5}\text{Cs}_{0.5}$ alloys, the phonon frequency decreases with increase in the average volume of the solid alloys. The experimental phonon frequencies of such alloys are not available in the literature for further comparison and write some concrete remarks. But, in the absence of experimental information such calculations may be considered as one of the guidelines for further investigations either theoretical or experimental. Hence, such study could be extended for the other types of binary alloys.

4. CONCLUSIONS

At the end, we concluded that the present model is successful in explaining the static and vibrational properties of equiatomic lithium based binary alloys and hence it could be explored for predicting the behavior of other such solid solutions. The comparison of present theoretical findings helps us to note that the binding of $A_{1-x}B_x$ ($A = \text{Li}$; $B = \text{Na, K, Rb, Cs}$) is comparable to the pure metals and hence it behaves like a solid metallic alloy. This can be confirmed by investigating its total crystal energy and heat of solution. The results of total crystal energy and heat of solution of the solid metallic alloys are under progress and will be communicated in future. From the present experience, we also conclude that it should be interesting to apply other local pseudopotentials for such comprehensive study to judge and confirm the wider applicability of the potential.

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